

Electronic Structure and Electron Dynamics in Two-Dimensional Materials

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Edmond Turcu

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Jens Christian Johannsen

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Felix Fromm

Christian Raidel

Samir Mammadov

Thomas Seyller



Søren Ulstrup



Jill Miwa



Jens Johannsen



Signe Grønberg

VILLUM FONDEN



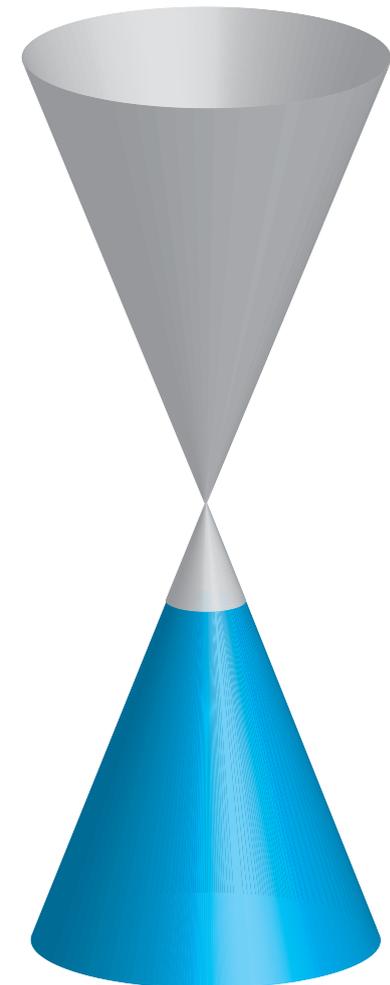
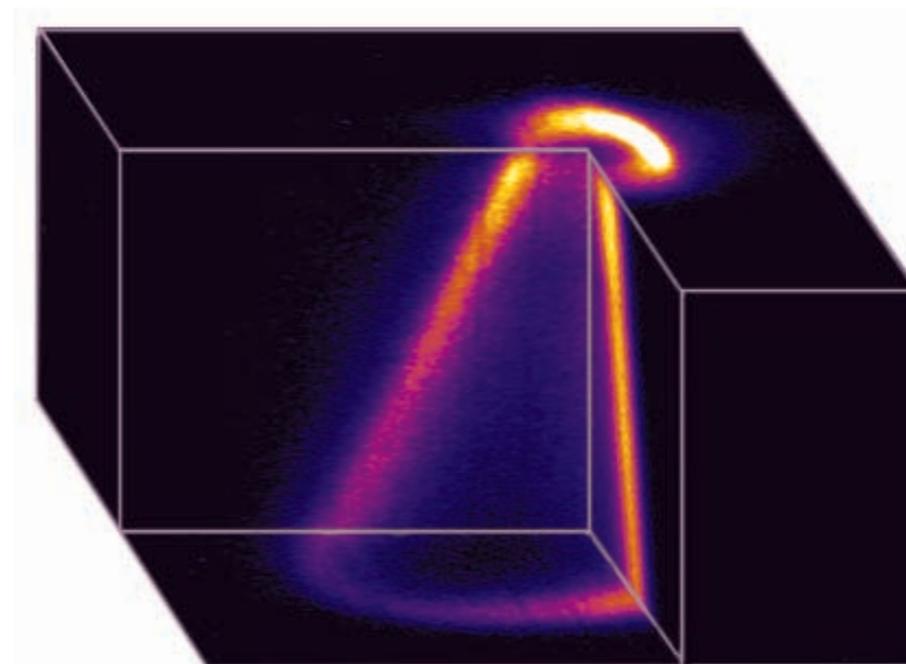
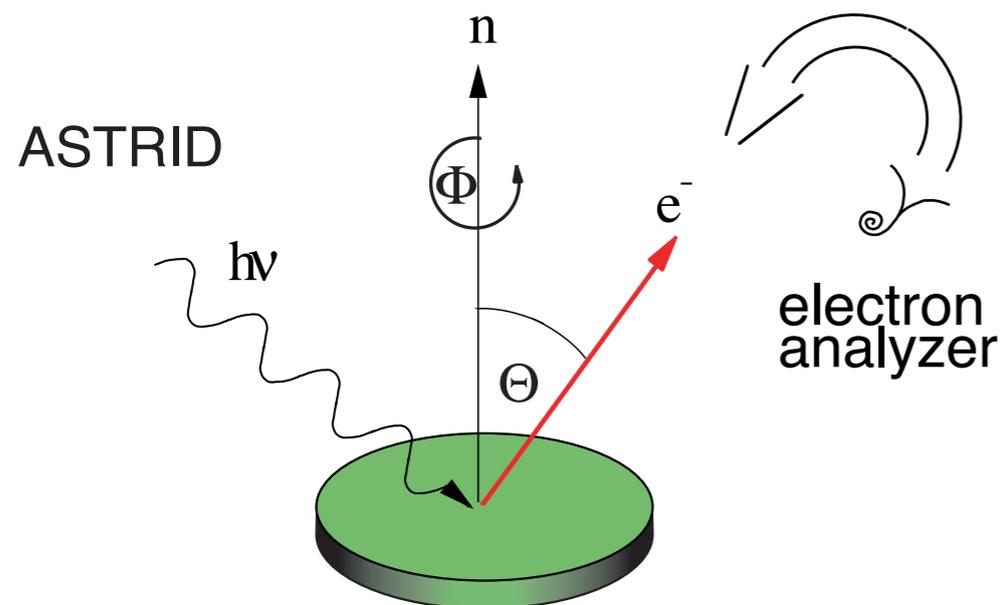
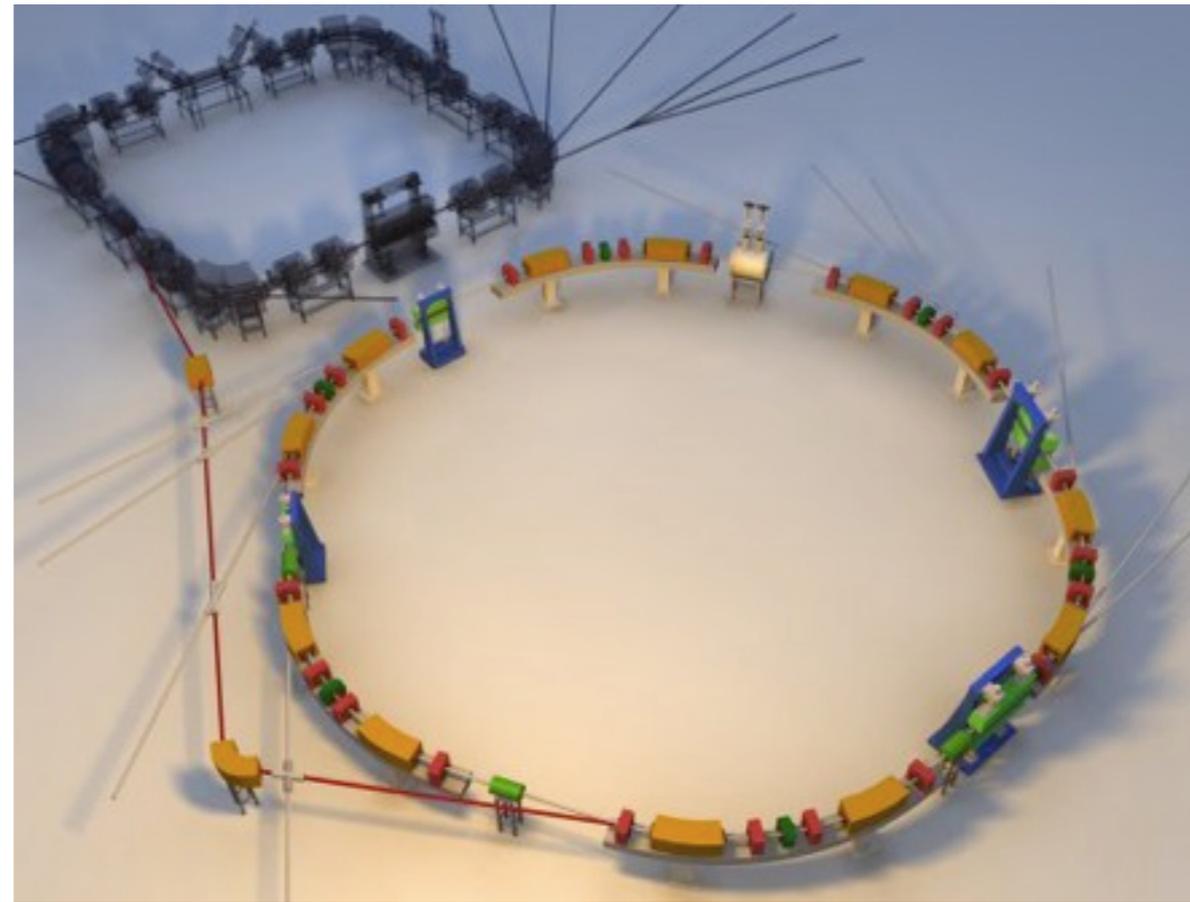
LUNDBECKFONDEN



DET FRIE
FORSKNINGSRÅD
DANISH COUNCIL
FOR INDEPENDENT
RESEARCH

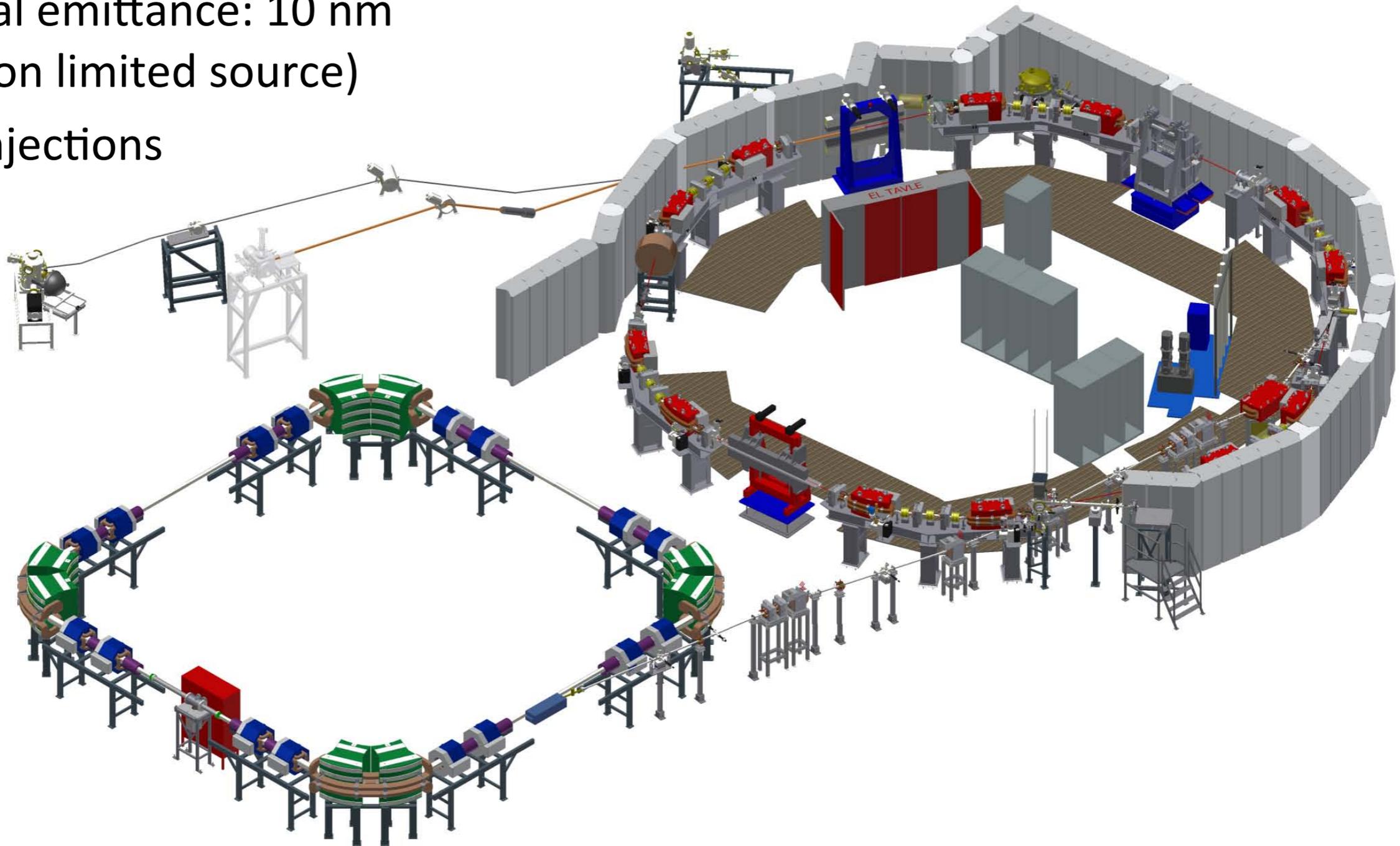
- modifying the properties of epitaxial graphene
- spin splitting in WSe_2 and single layer MoS_2
- ultrafast carrier dynamics

angle-resolved photoemission (ARPES): a direct view at the band structure

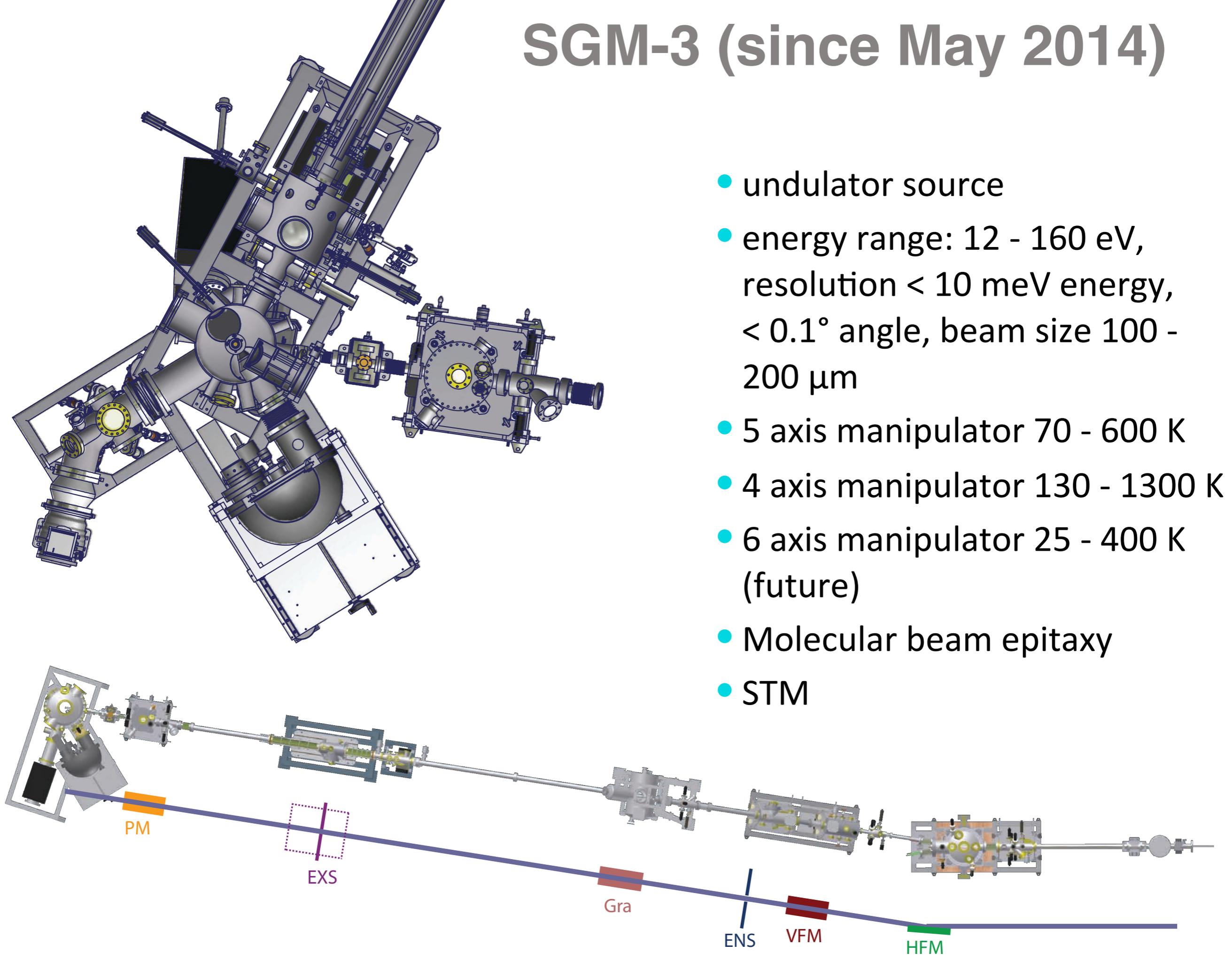


ASTRID2 (since 2013)

- 3rd generation source
- 580 MeV energy
- horizontal emittance: 10 nm (diffraction limited source)
- top-up injections

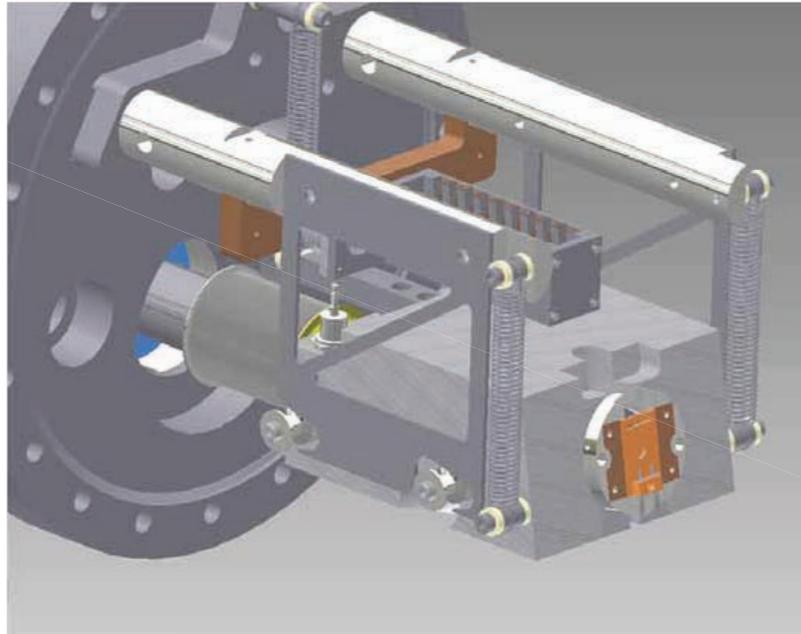


SGM-3 (since May 2014)



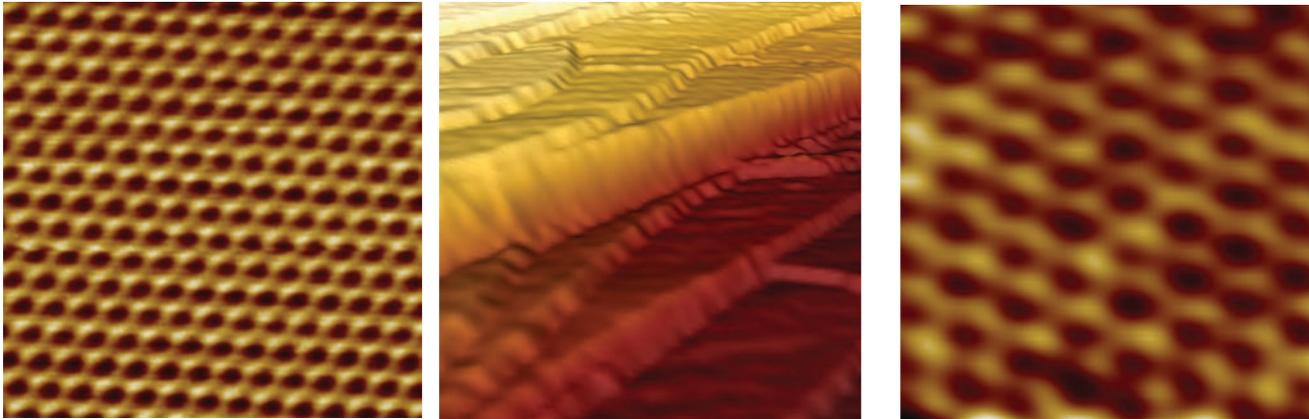
SGM-3

in-situ STM



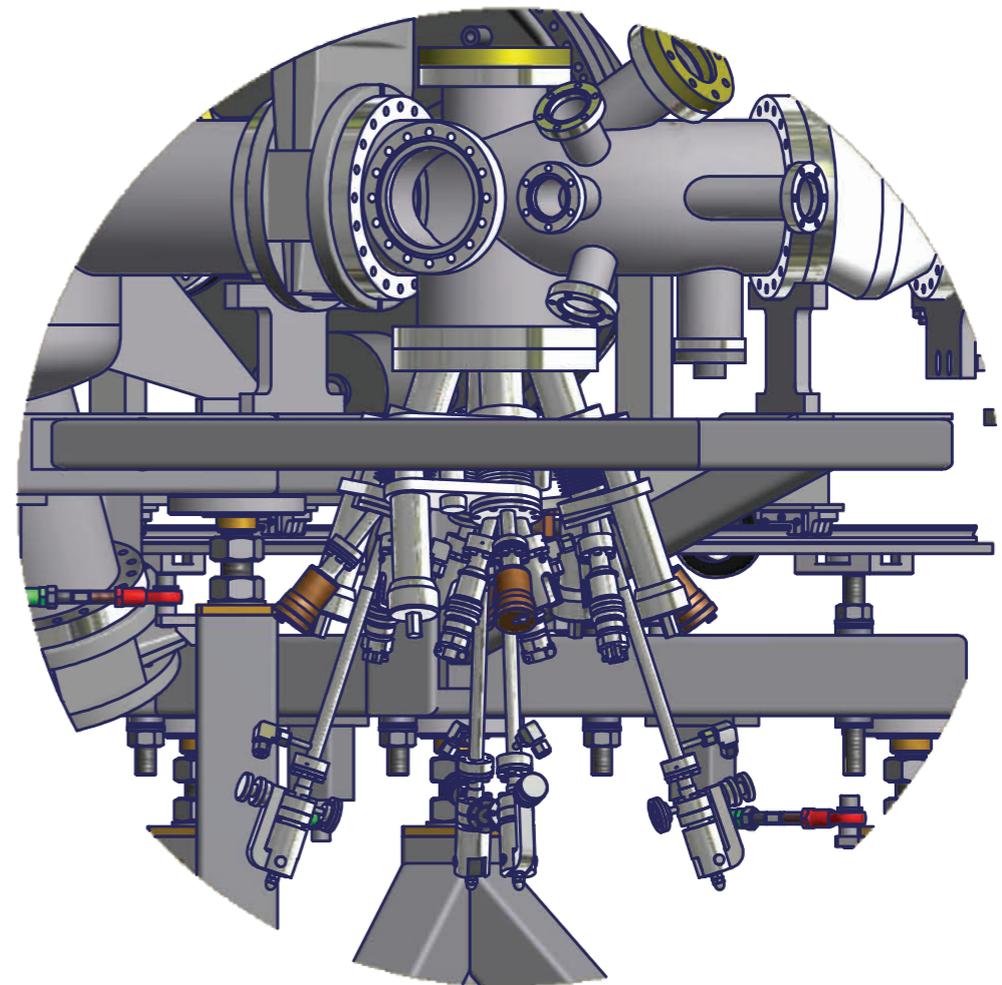
HOPG

Ag(111)



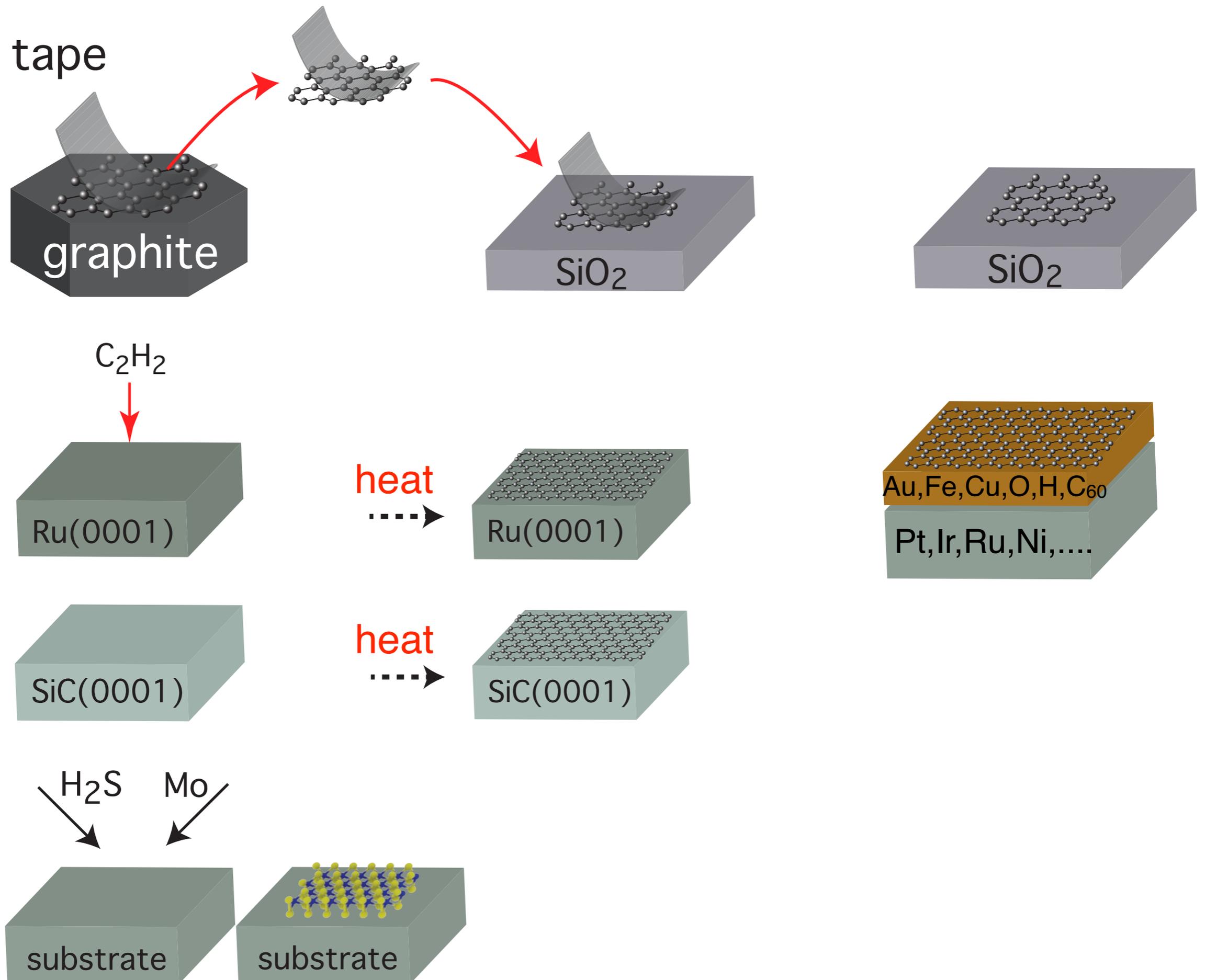
atomic resolution with 3 turbo pumps and closed-cycle cooler running

MBE chamber



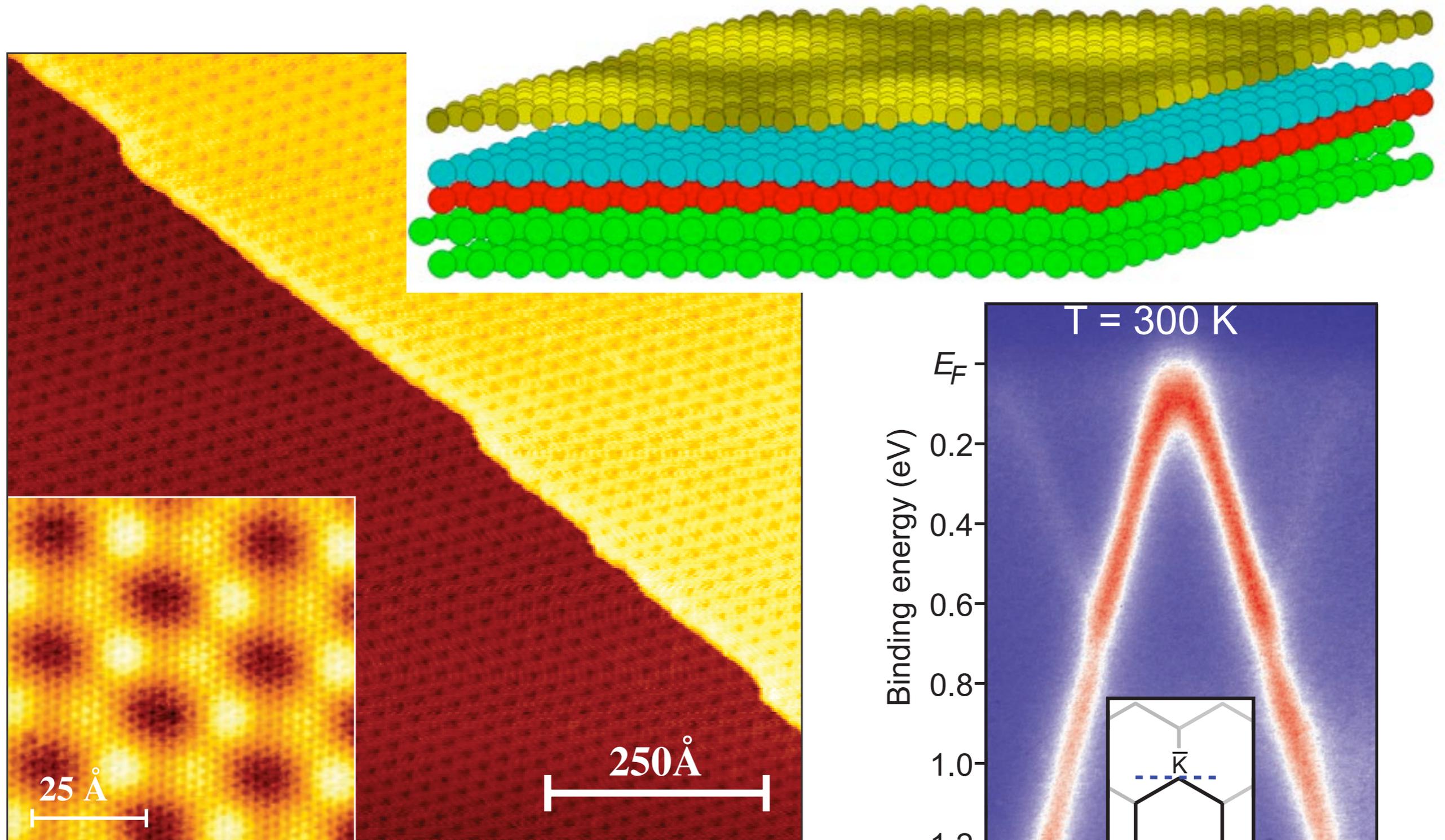
4 evaporators

epitaxial 2D materials



- **modifying the properties of epitaxial graphene**
- spin splitting in WSe_2 and single layer MoS_2
- ultrafast carrier dynamics

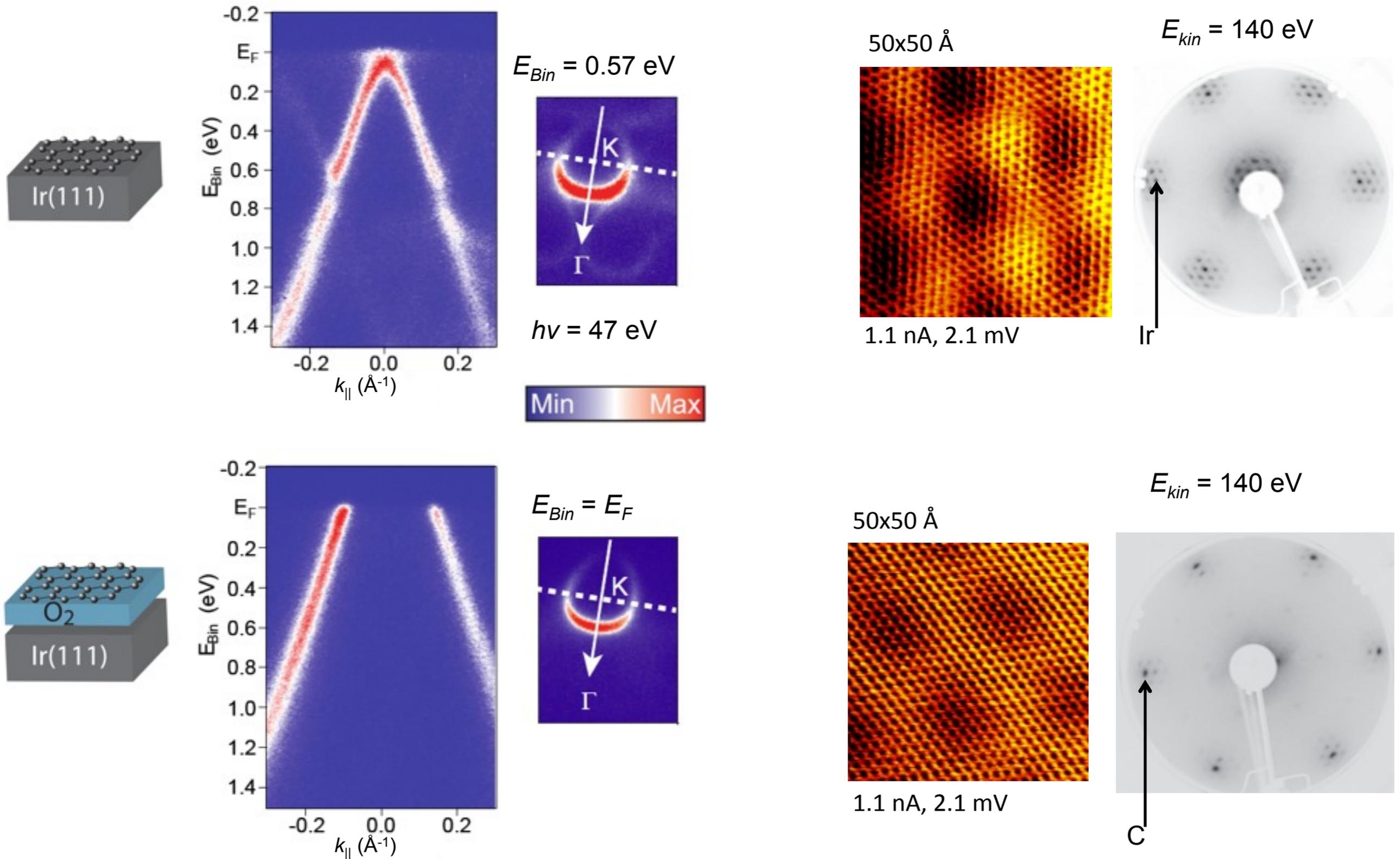
epitaxial graphene: here on Ir(111)



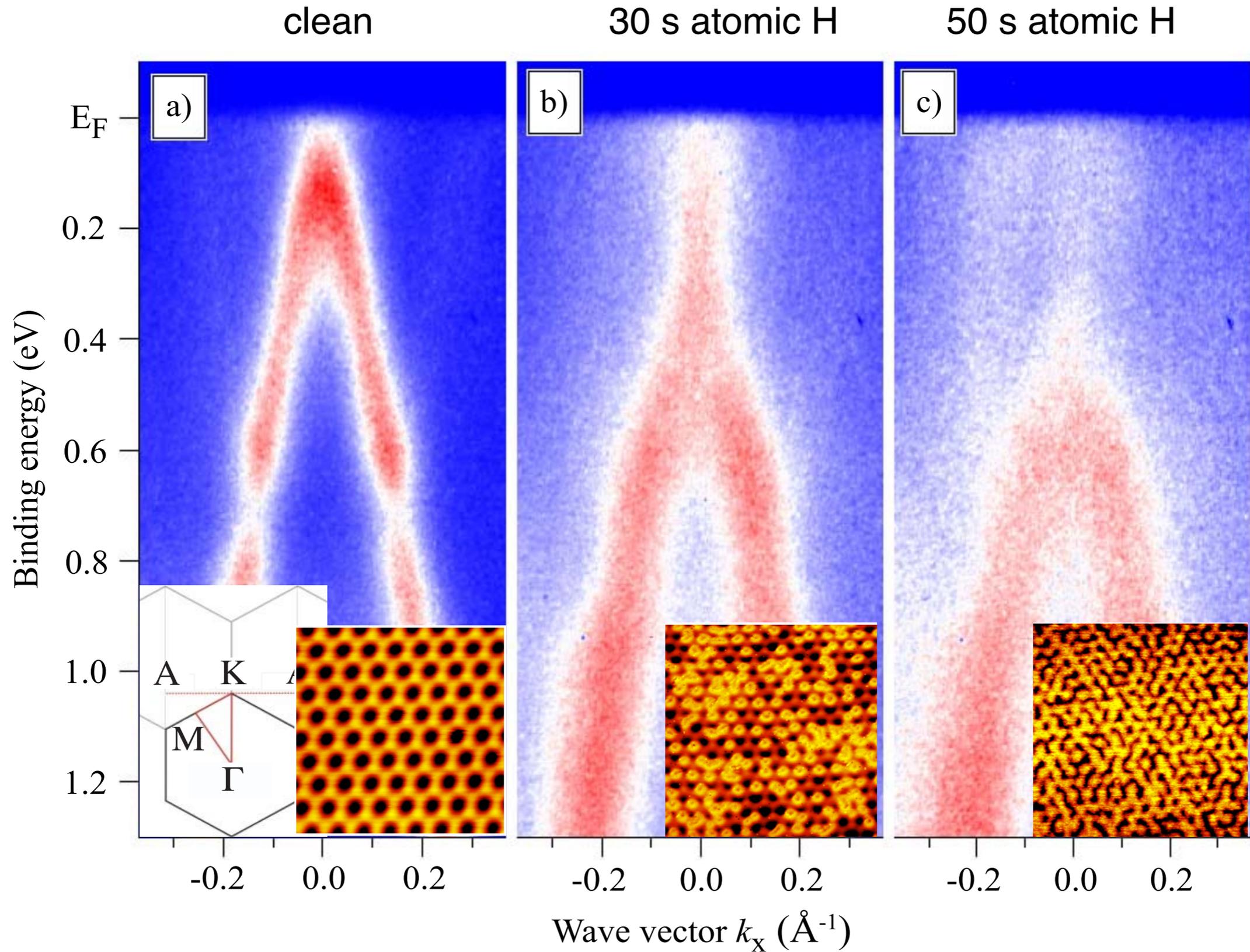
N'Diaye *et al.* New Journal of Physics **10**, 043033 (2008)

Pletikoscic *et al.*, Phys. Rev. Lett. **102**, 05608 (2009)

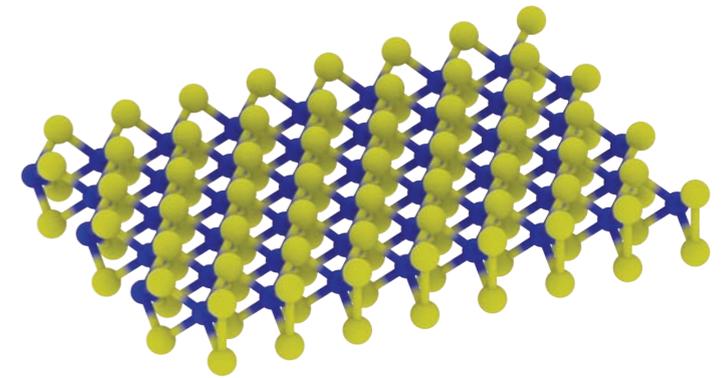
quasi-free standing graphene: O intercalation



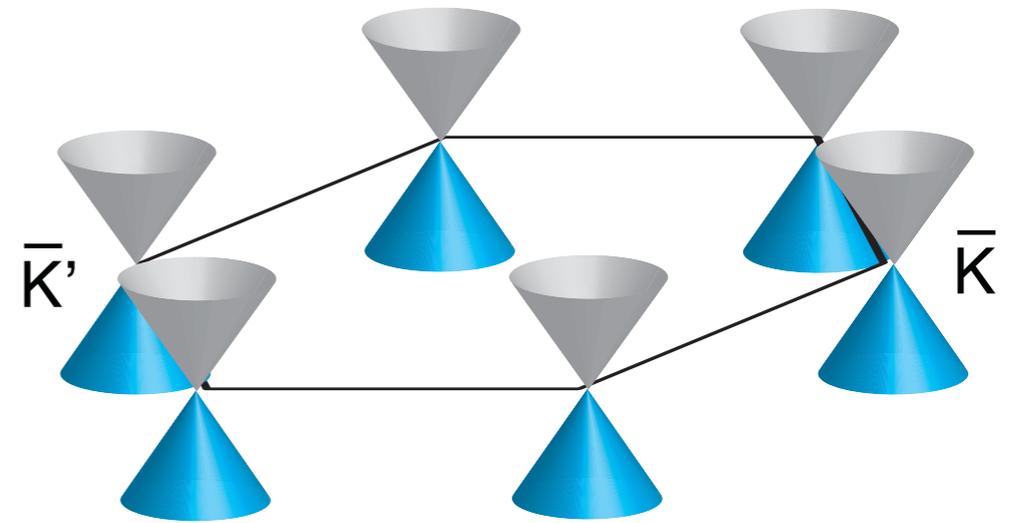
Electronic structure by ARPES



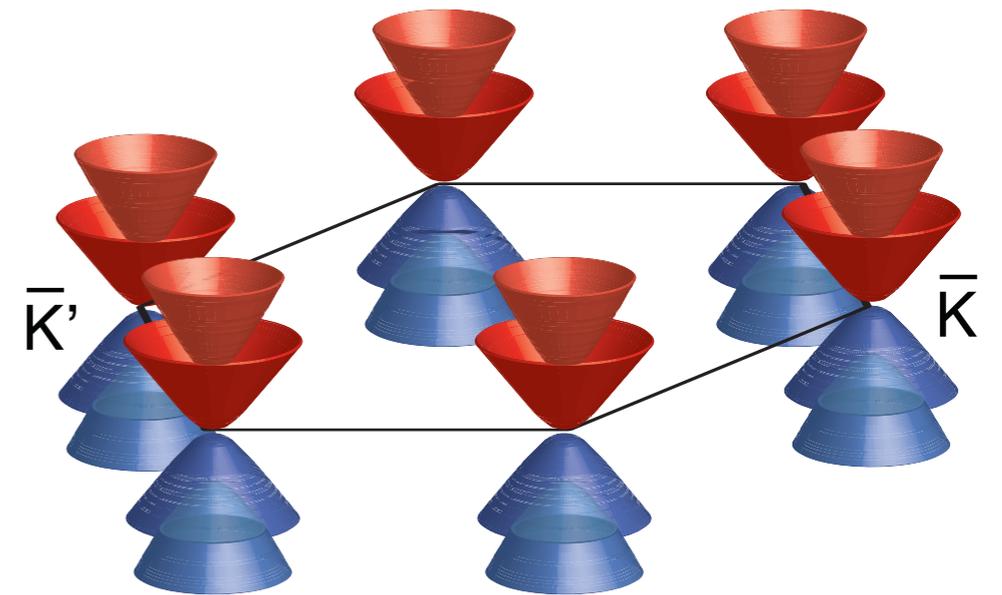
- modifying the properties of epitaxial graphene
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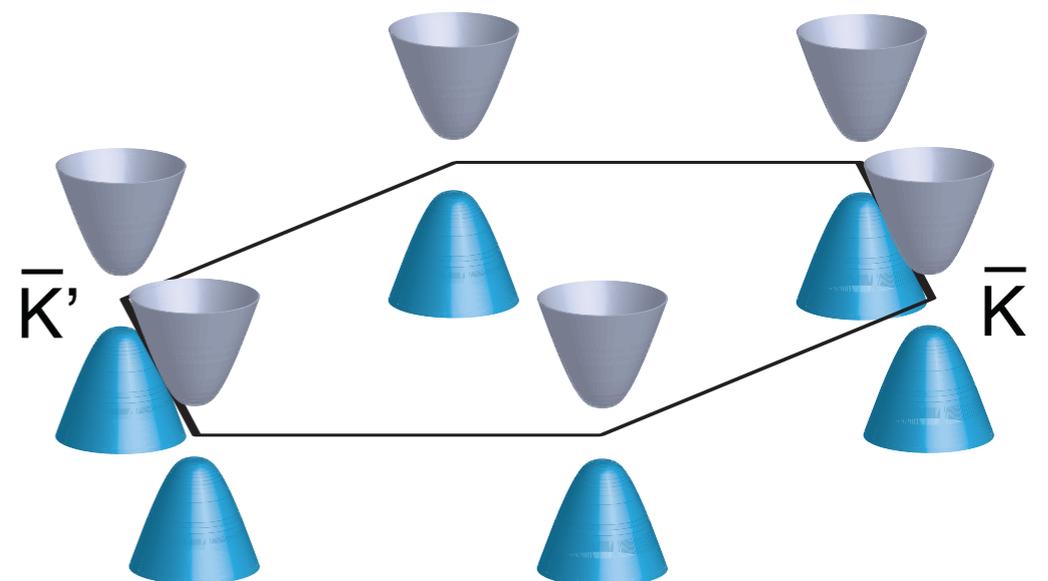
graphene



bilayer graphene
(in weak electric field)

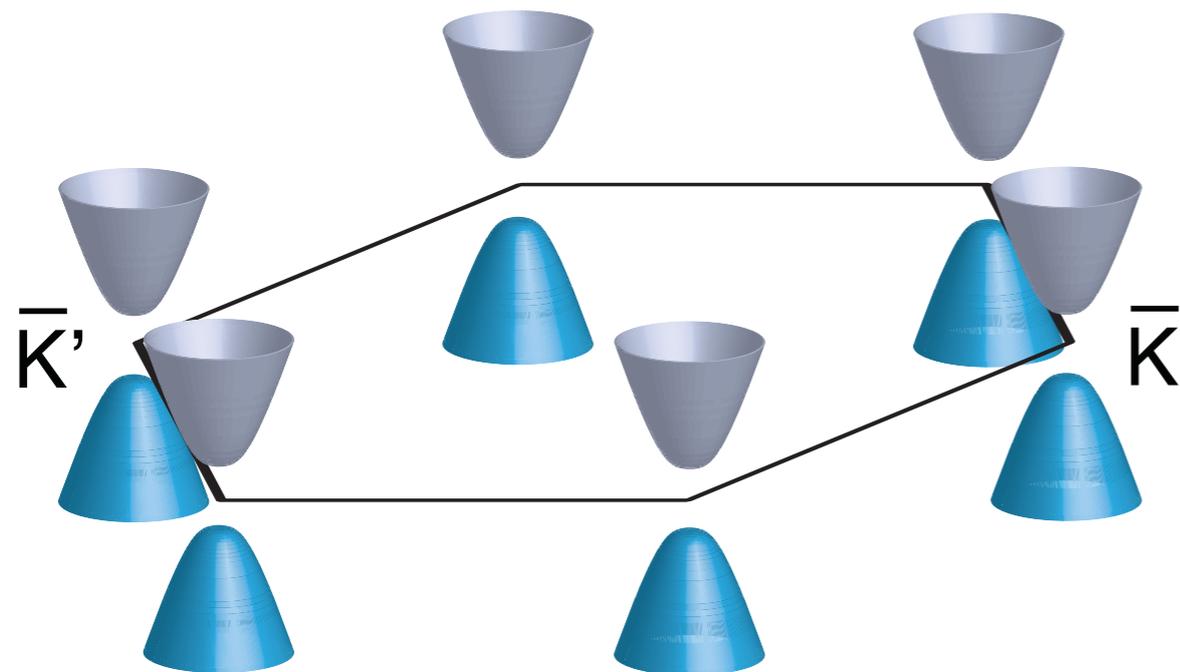


single layer MoS_2

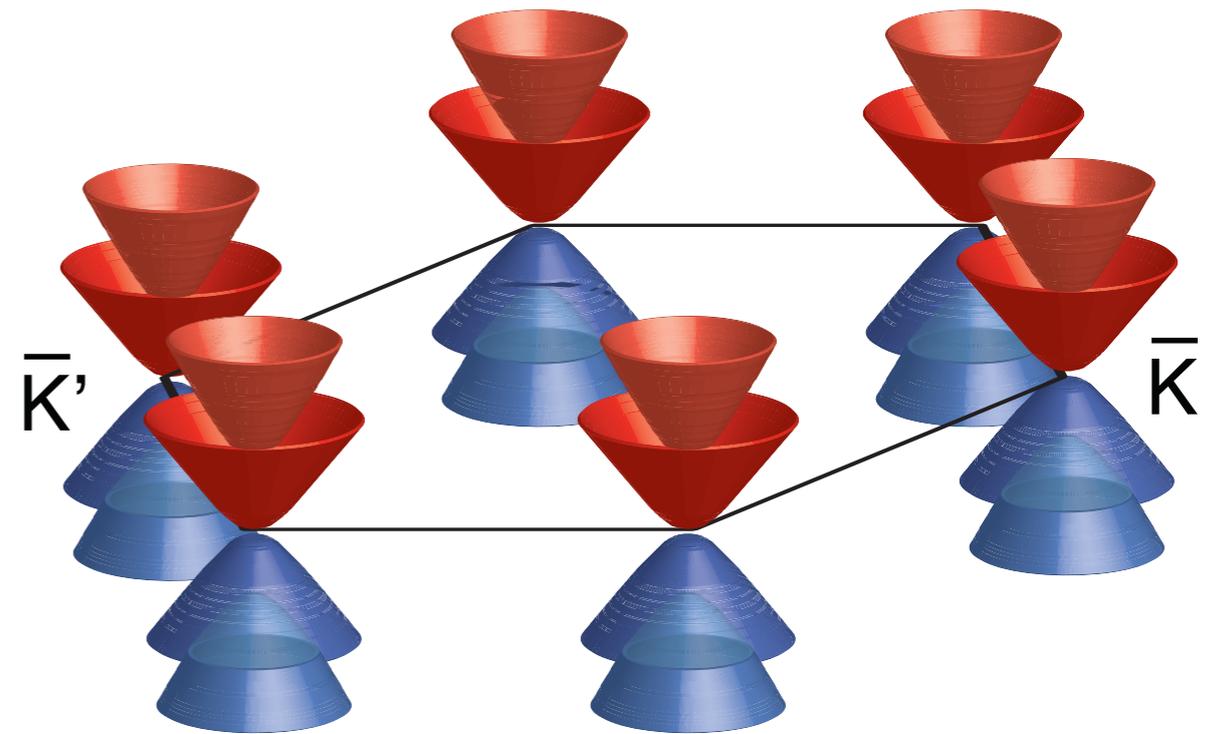


new degrees of freedom: valley and layer pseudo spin

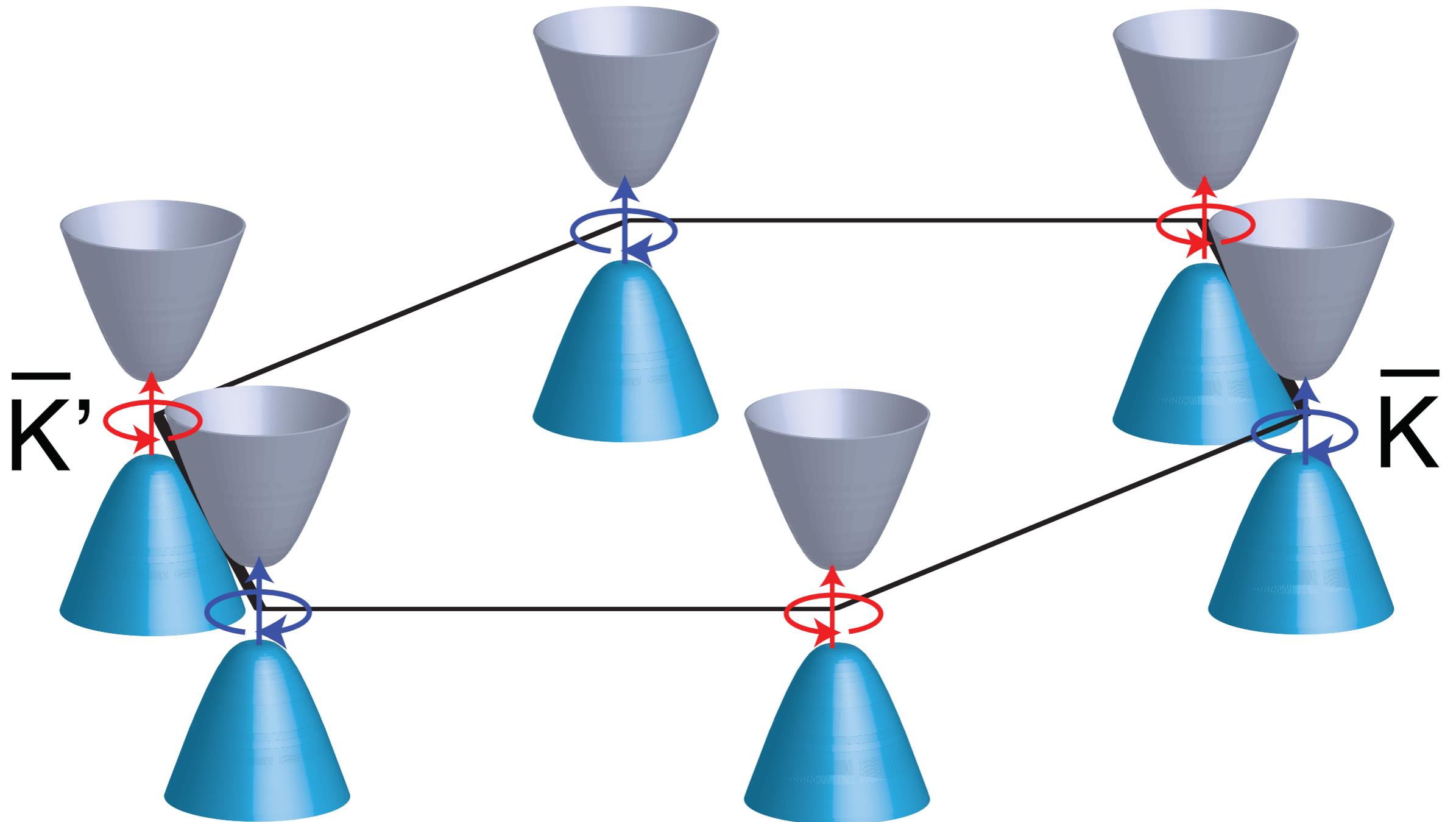
single layer MoS₂



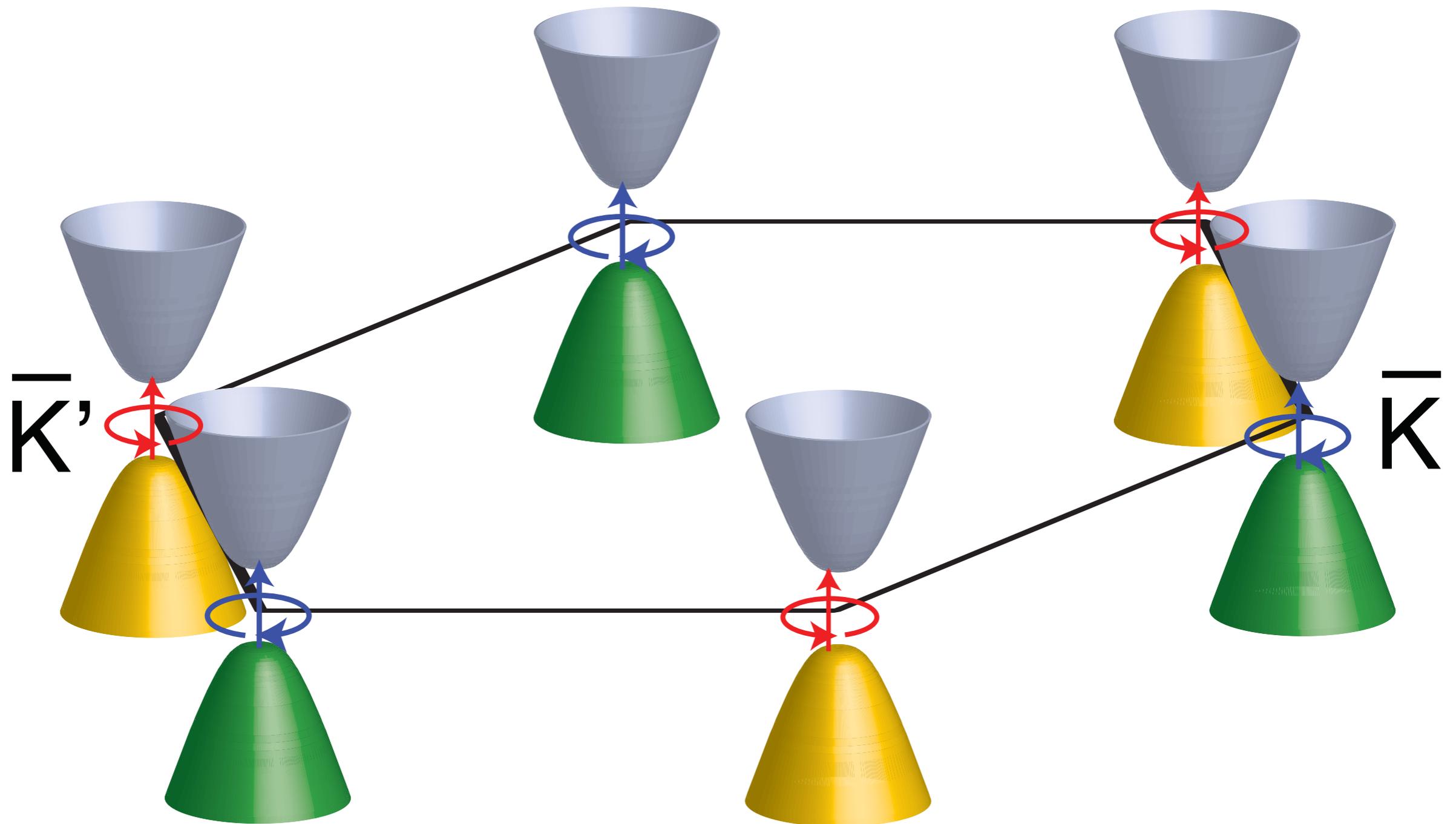
bilayer graphene



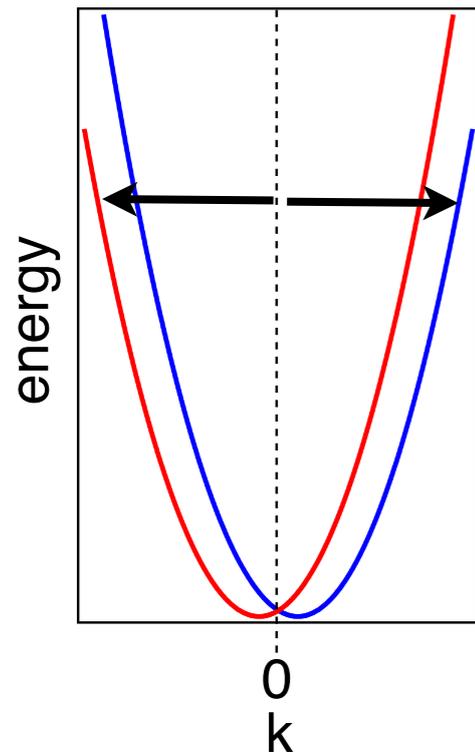
new degrees of freedom: (pseudo) spin, valley, layer



new degrees of freedom: (pseudo) spin, valley, layer

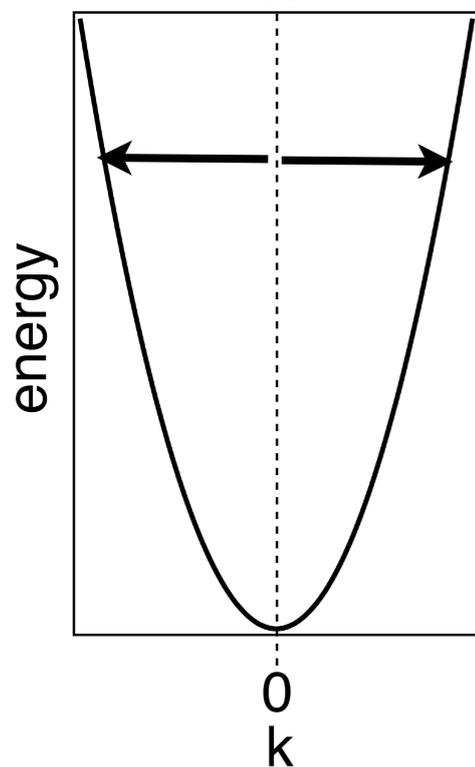


spin splitting of the band structure



time reversal symmetry:

$$\epsilon(\vec{k}, \uparrow) = \epsilon(-\vec{k}, \downarrow)$$

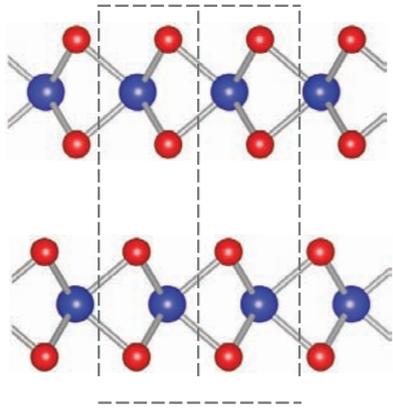
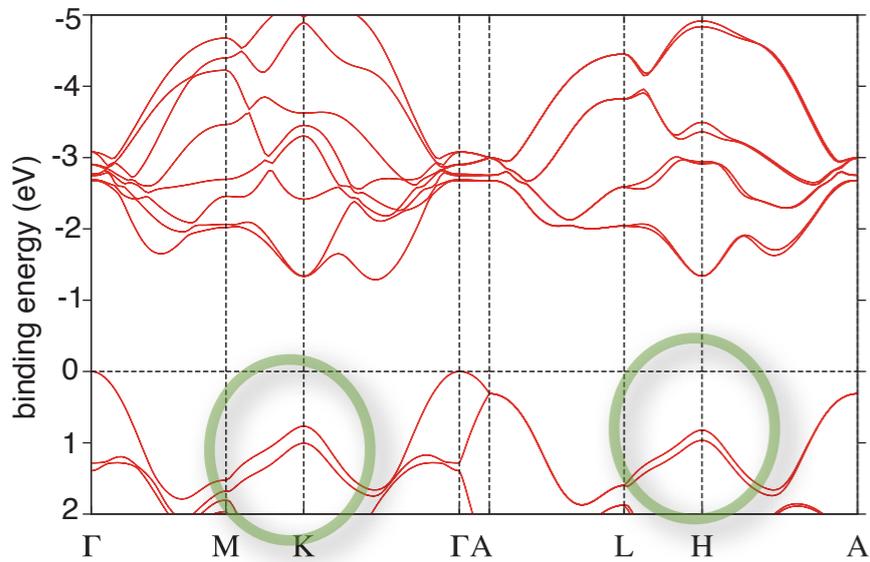


+inversion symmetry:

$$\epsilon(\vec{k}, \uparrow) = \epsilon(-\vec{k}, \uparrow)$$

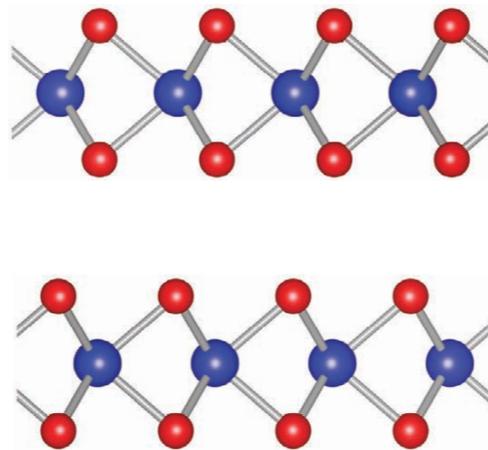
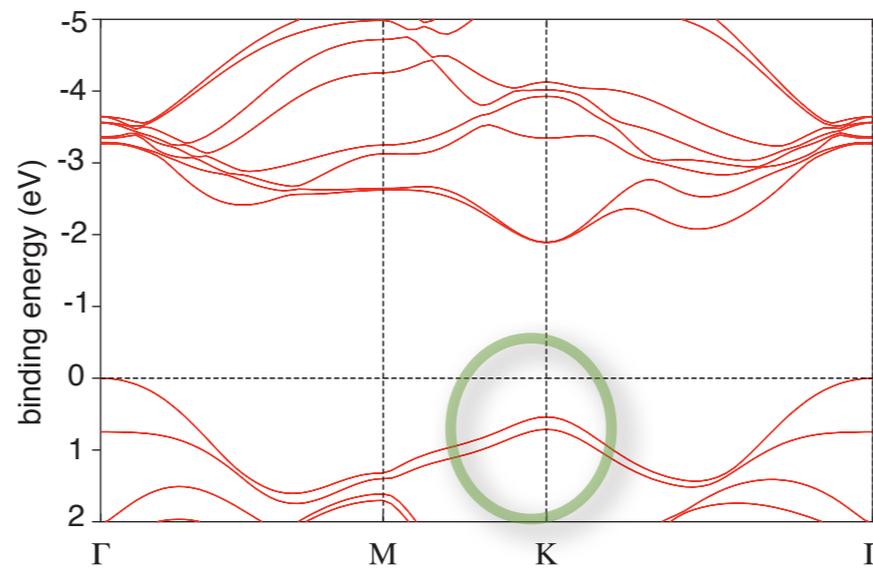
spin structure in MoS₂

bulk (2H)



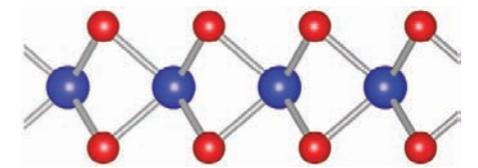
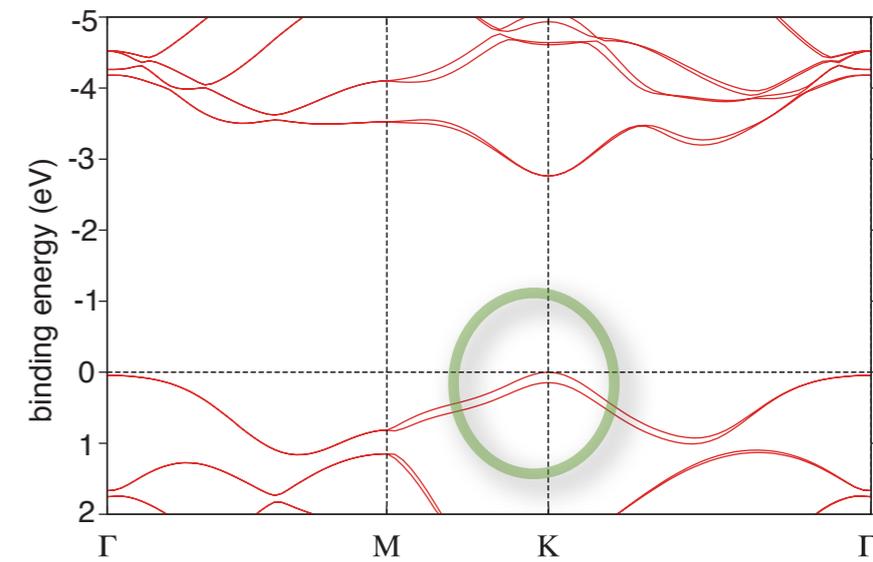
indirect band gap
inversion symmetry
no spin splitting

bilayer layer



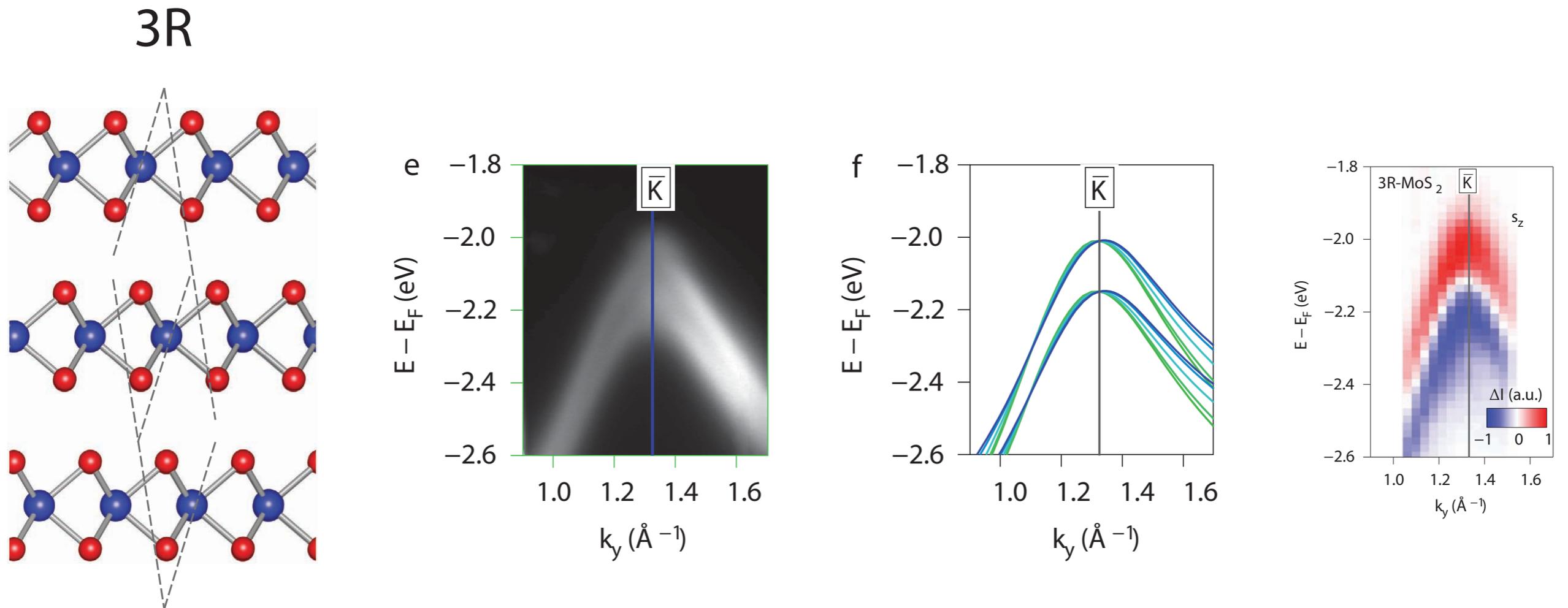
indirect band gap
inversion symmetry
no spin splitting

monolayer

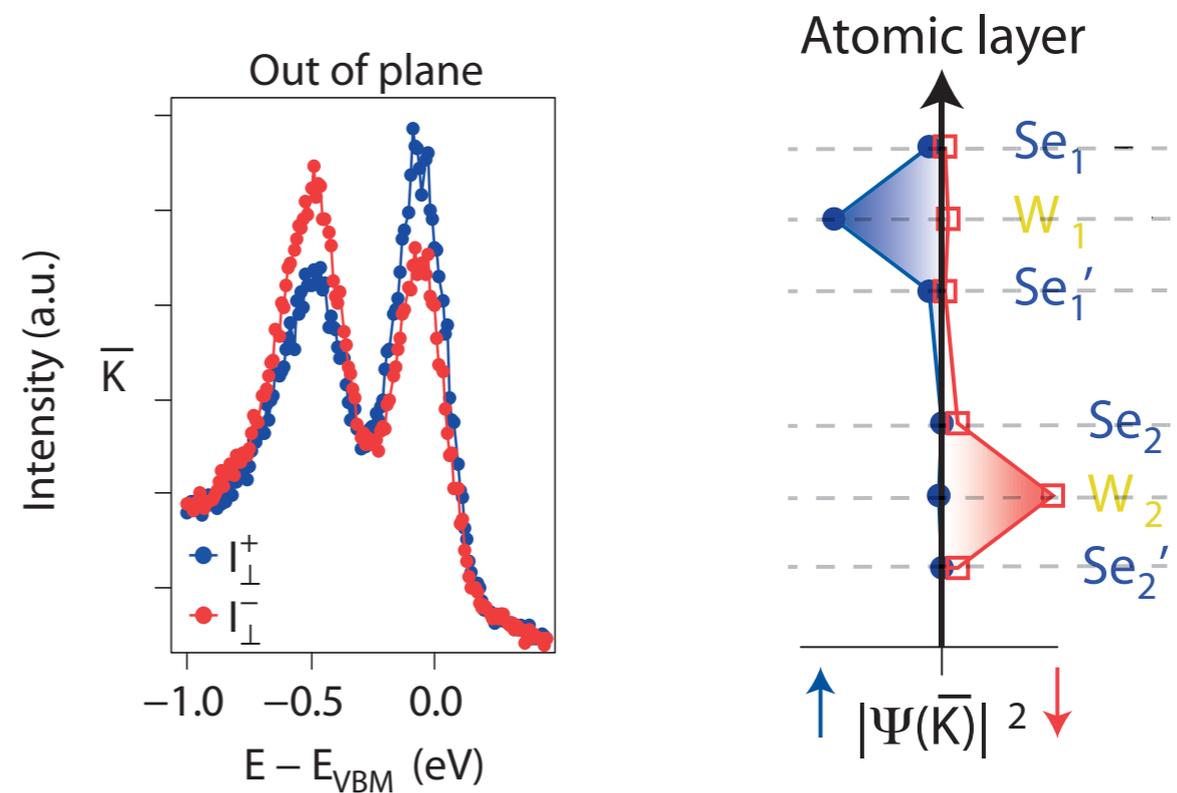
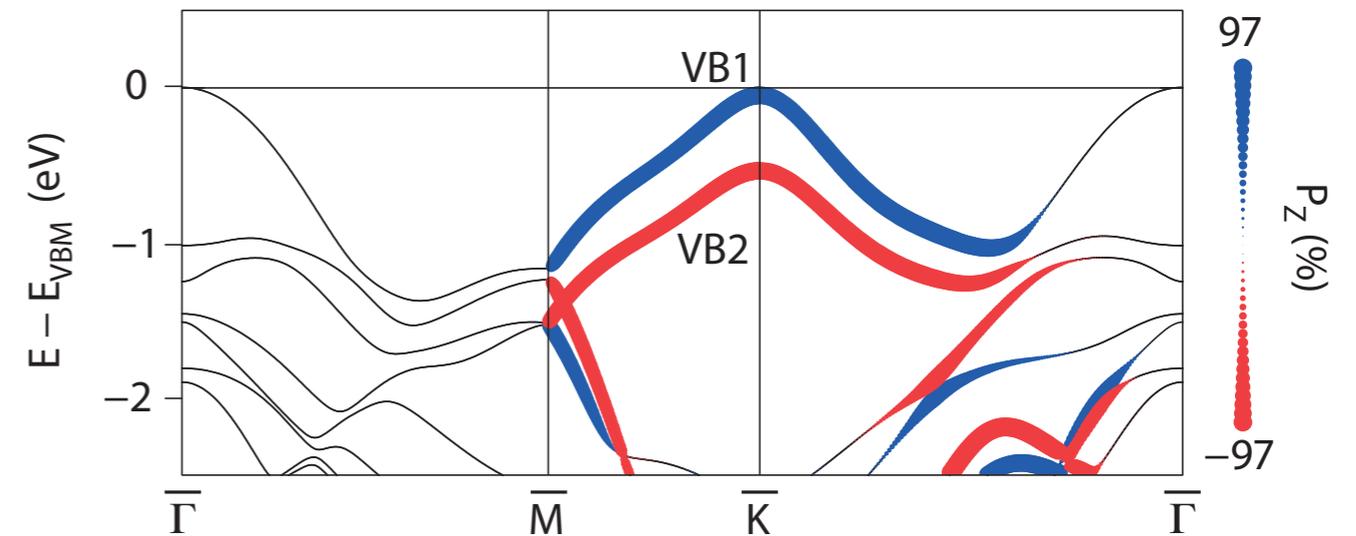
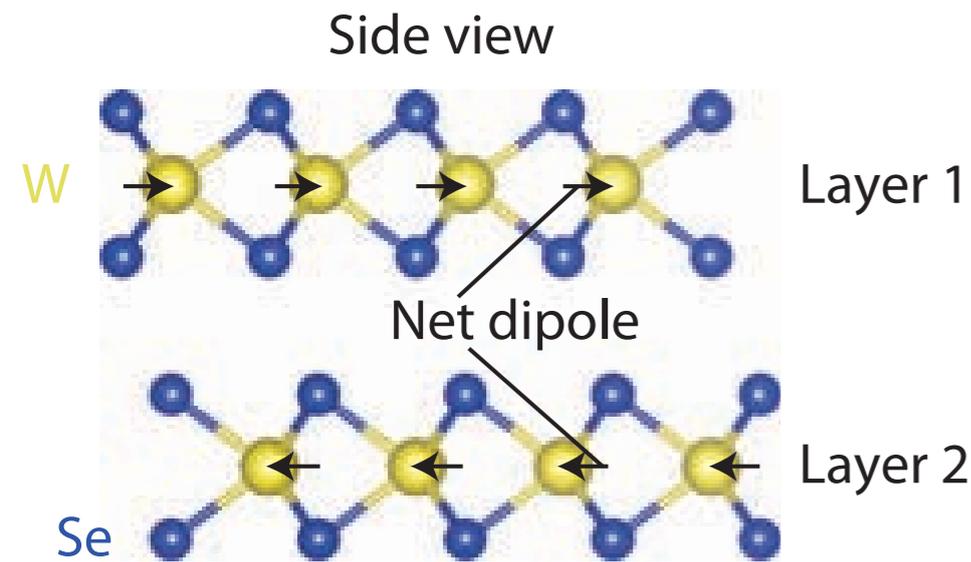


direct band gap
no inversion symmetry
spin splitting

spin polarization in bulk MoS₂: breaking the inversion symmetry



spin polarization in bulk 2H-WSe₂: locally breaking the inversion symmetry

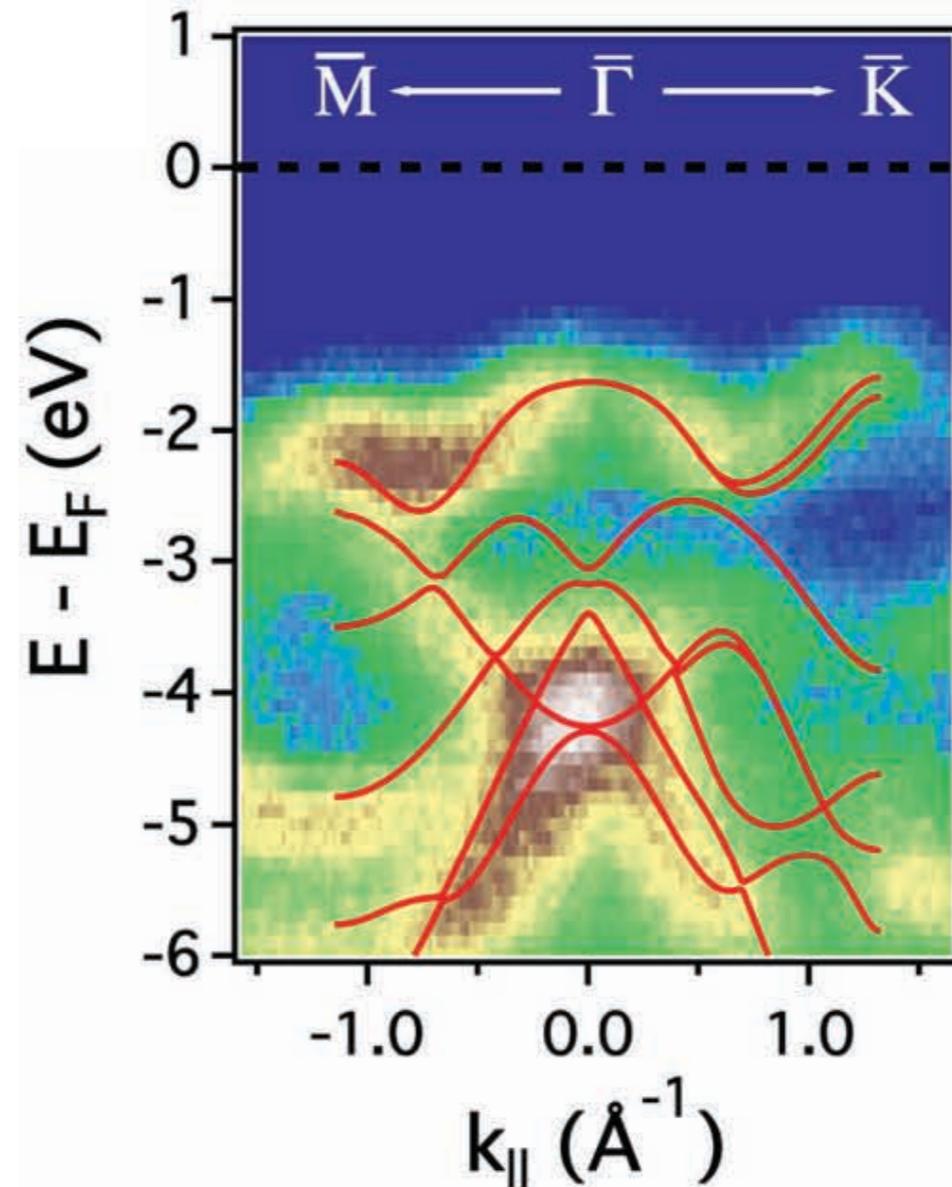
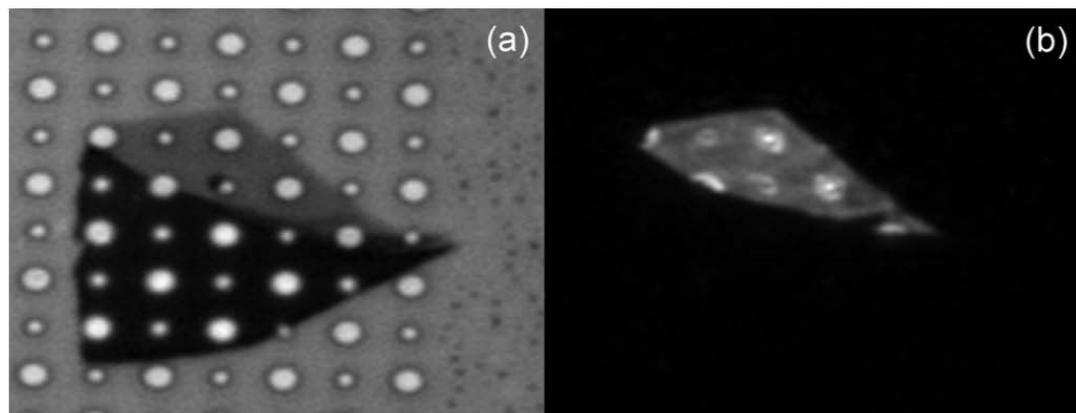
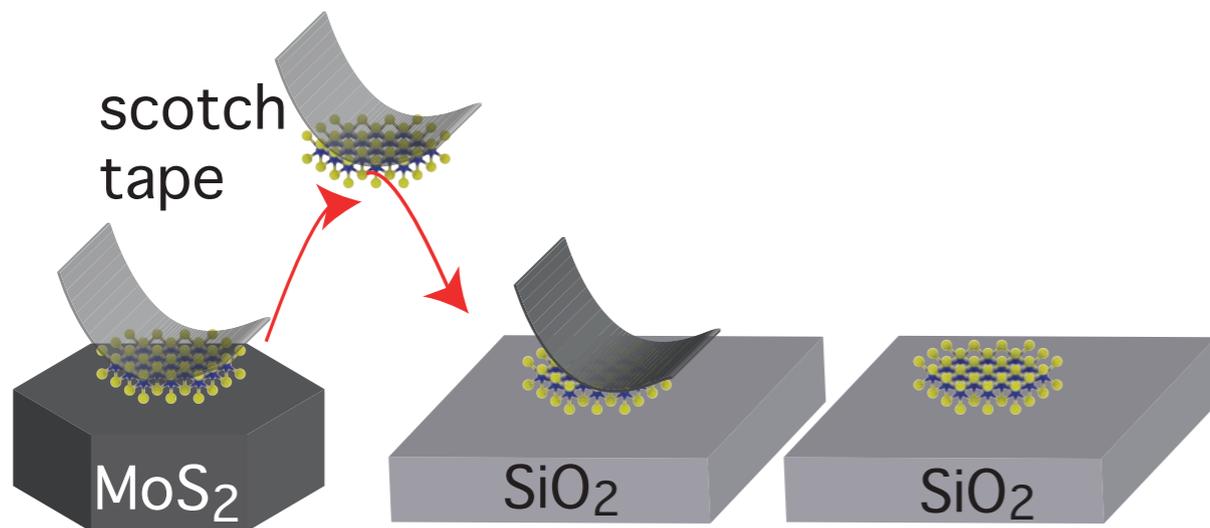


J. M Riley *et al.*, Nature Physics **10**, 835 (2014)

prediction by X. Zhang *et al.*, Nature Physics **10**, 387 (2014)

making single-layer MoS₂

- direct band gap
- spin-orbit split top of VB (predicted to be 150 meV)



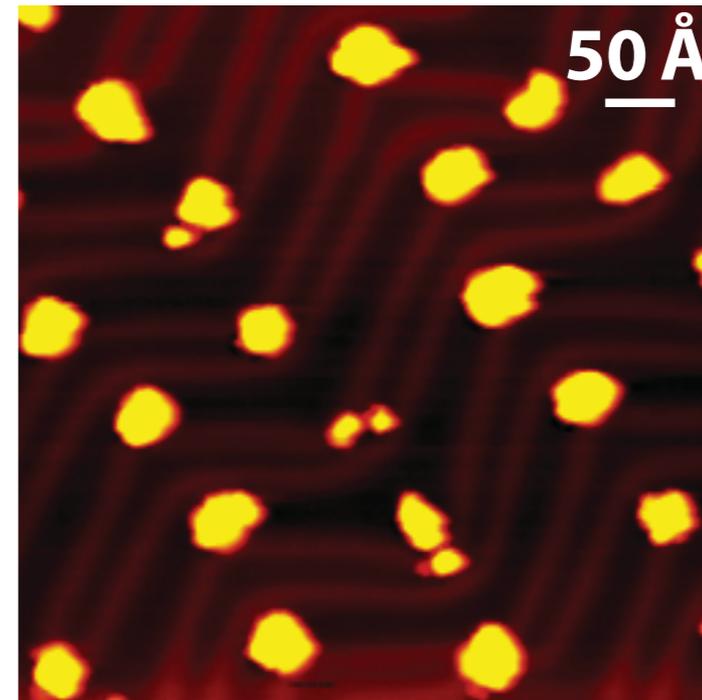
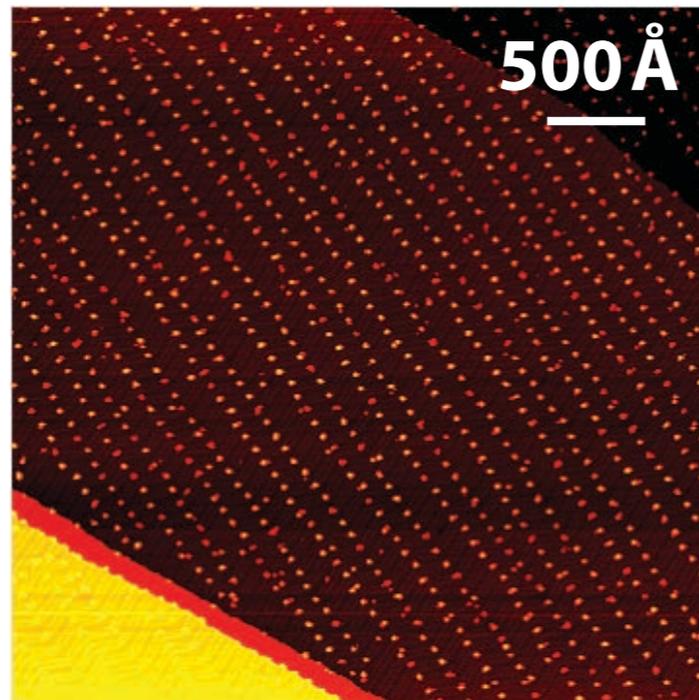
Wencan Jin *et al.*, PRL **111**, 106801 (2013)

Kin Fai Mak *et al.*, PRL **105**, 136805 (2010)

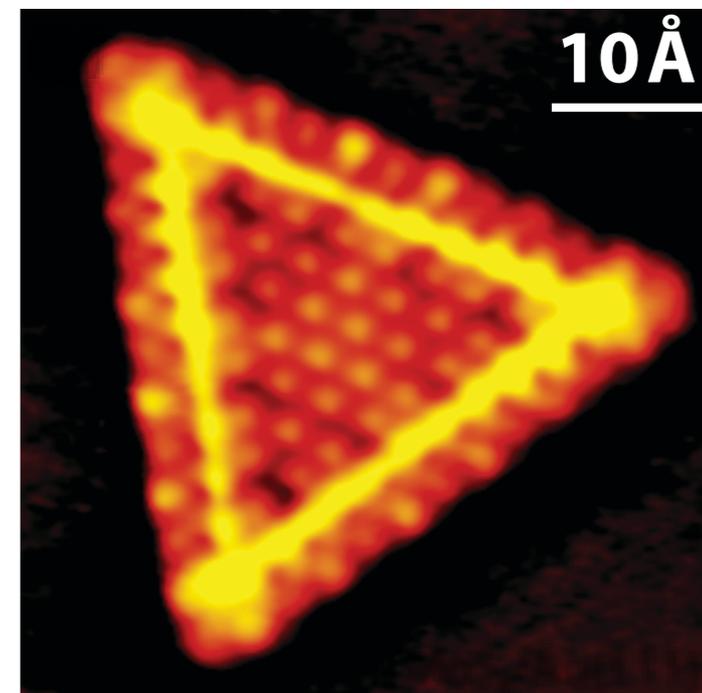
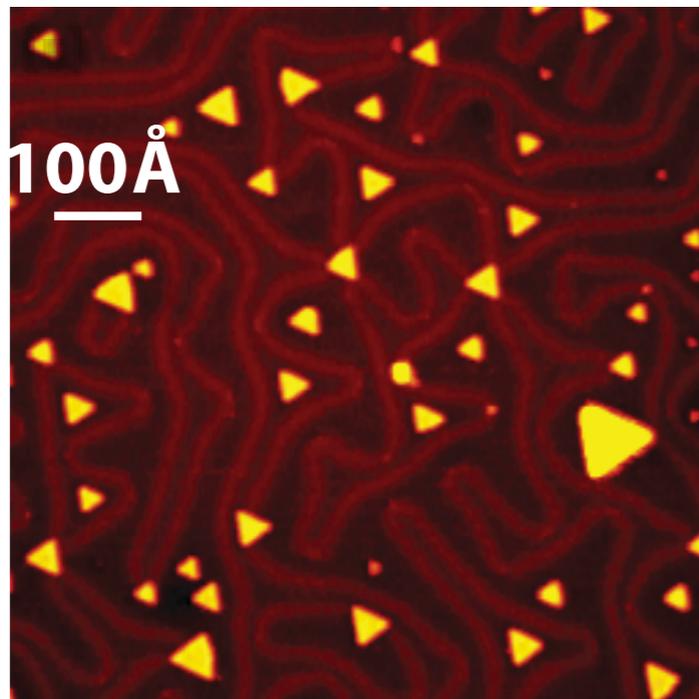
Andrea Splendiani *et al.*, Nano Lett. **4**, 1271 (2010)

creating epitaxial single-layer MoS₂

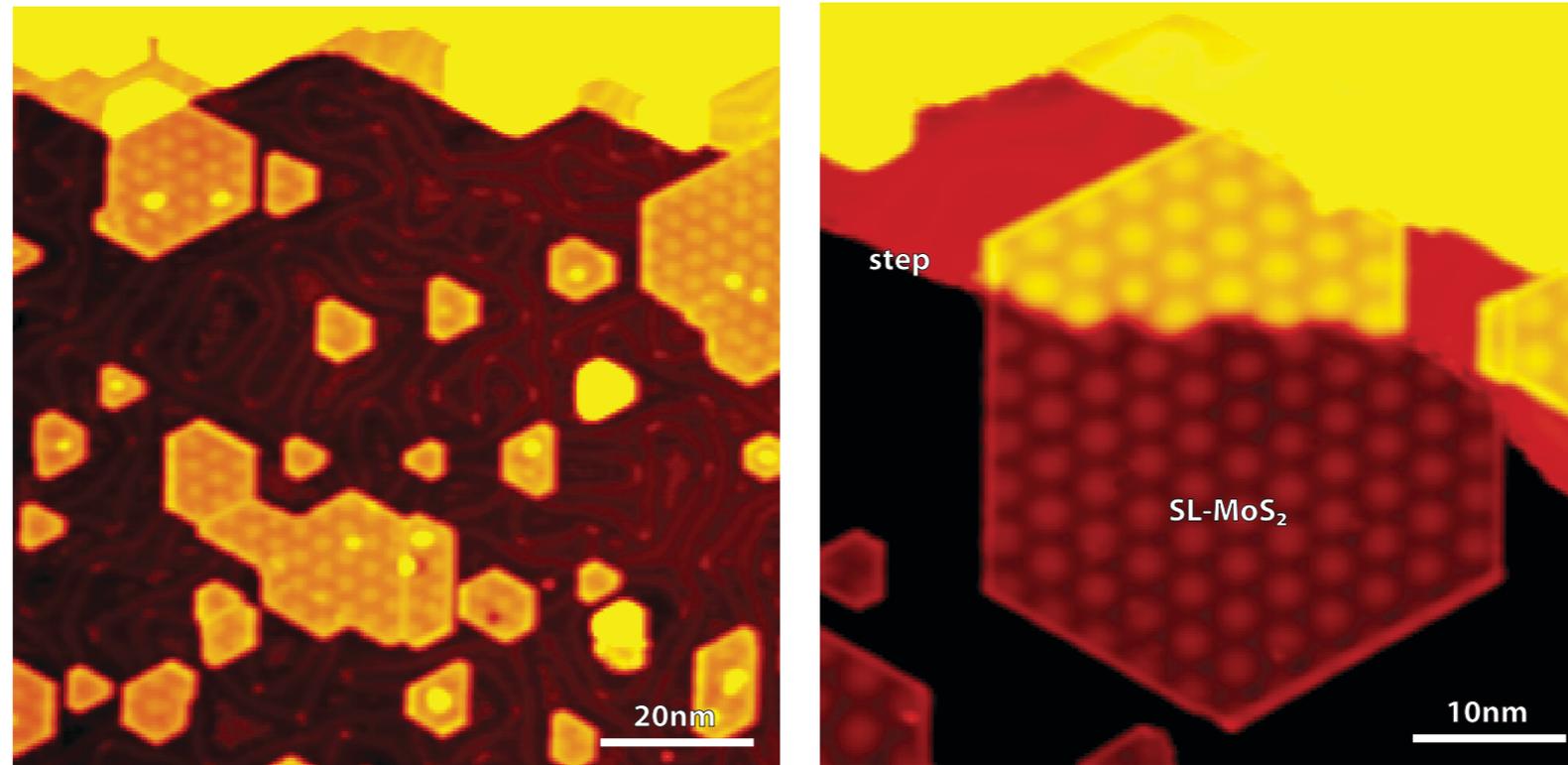
Mo clusters on Au(111)



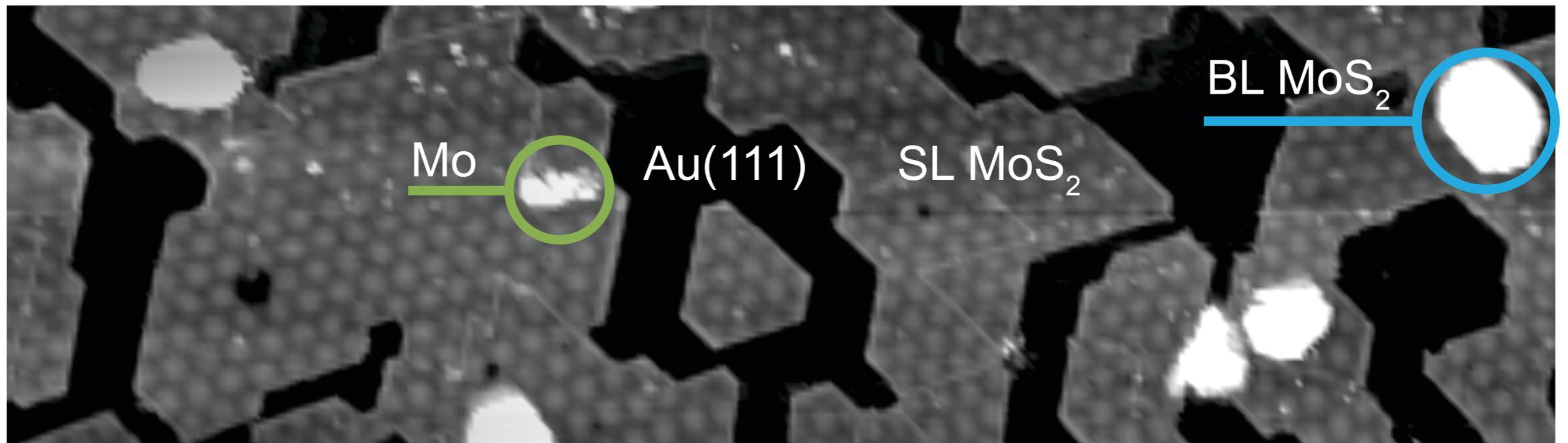
MoS₂ clusters on Au(111)



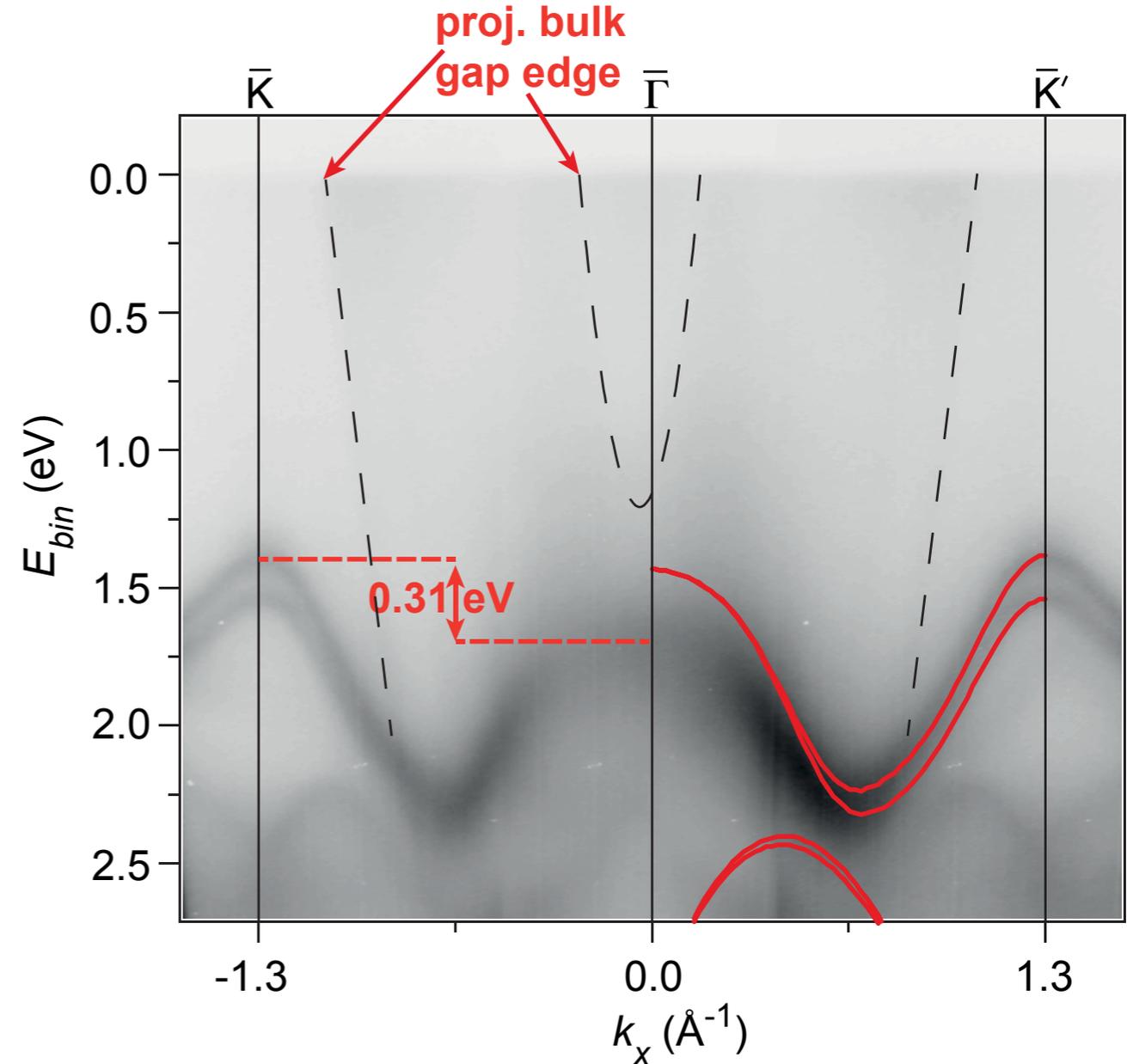
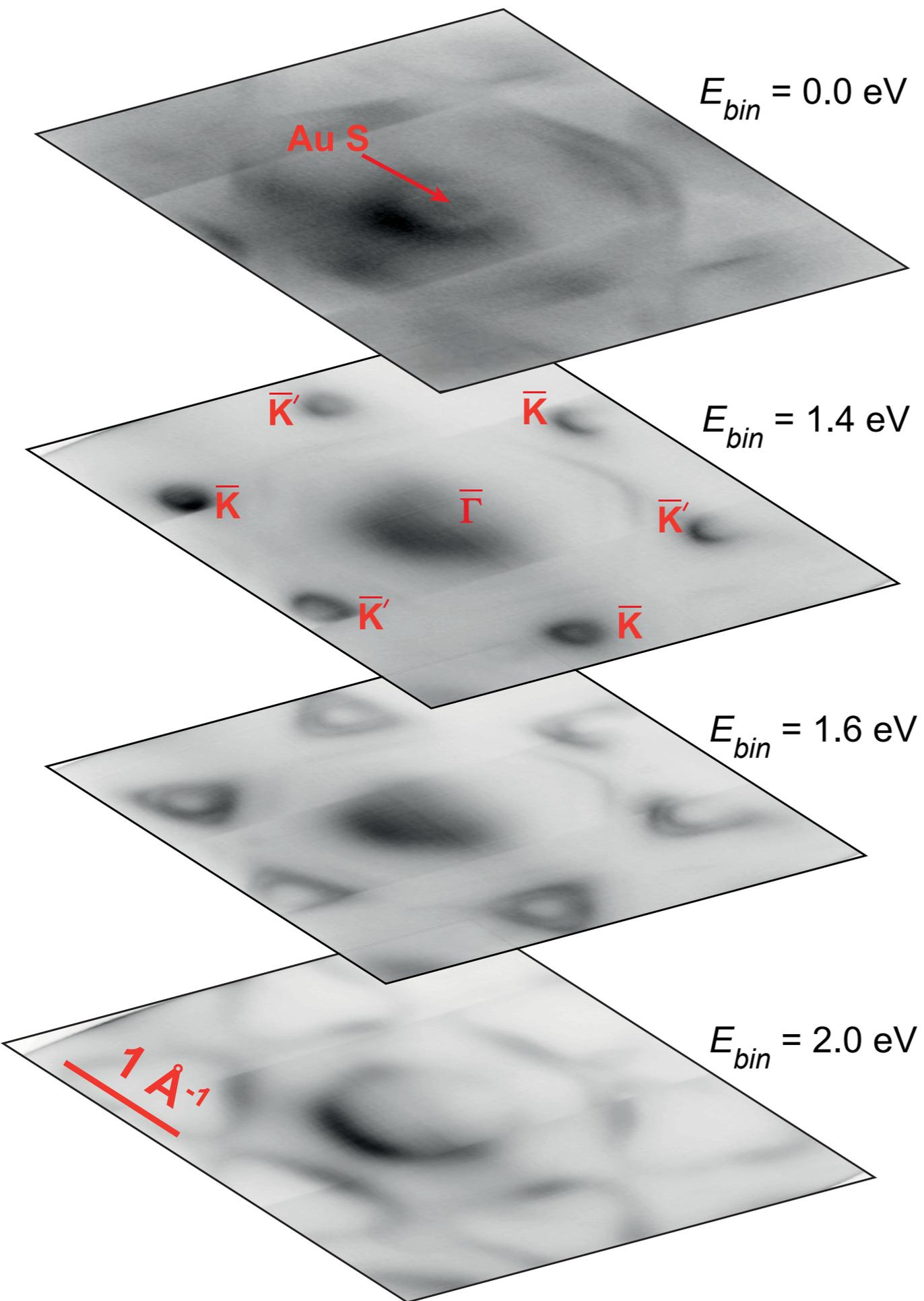
creating epitaxial single-layer MoS₂



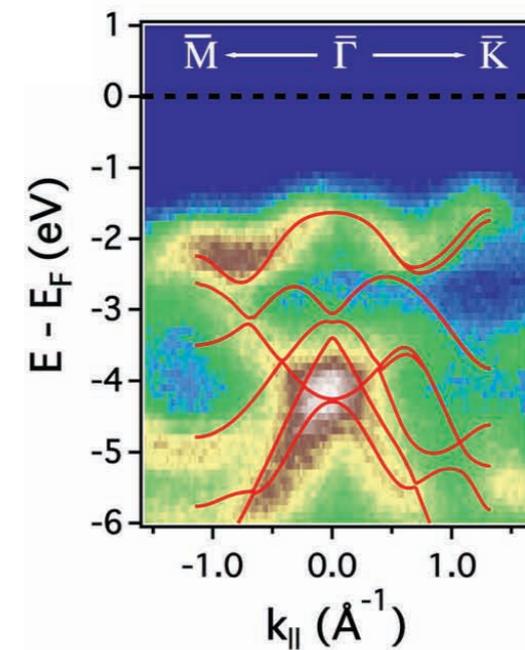
Signe G. Sørensen *et al.*, ACS Nano **8**, 6788 (2014)



Signe G. Sørensen *et al.*, unpublished results

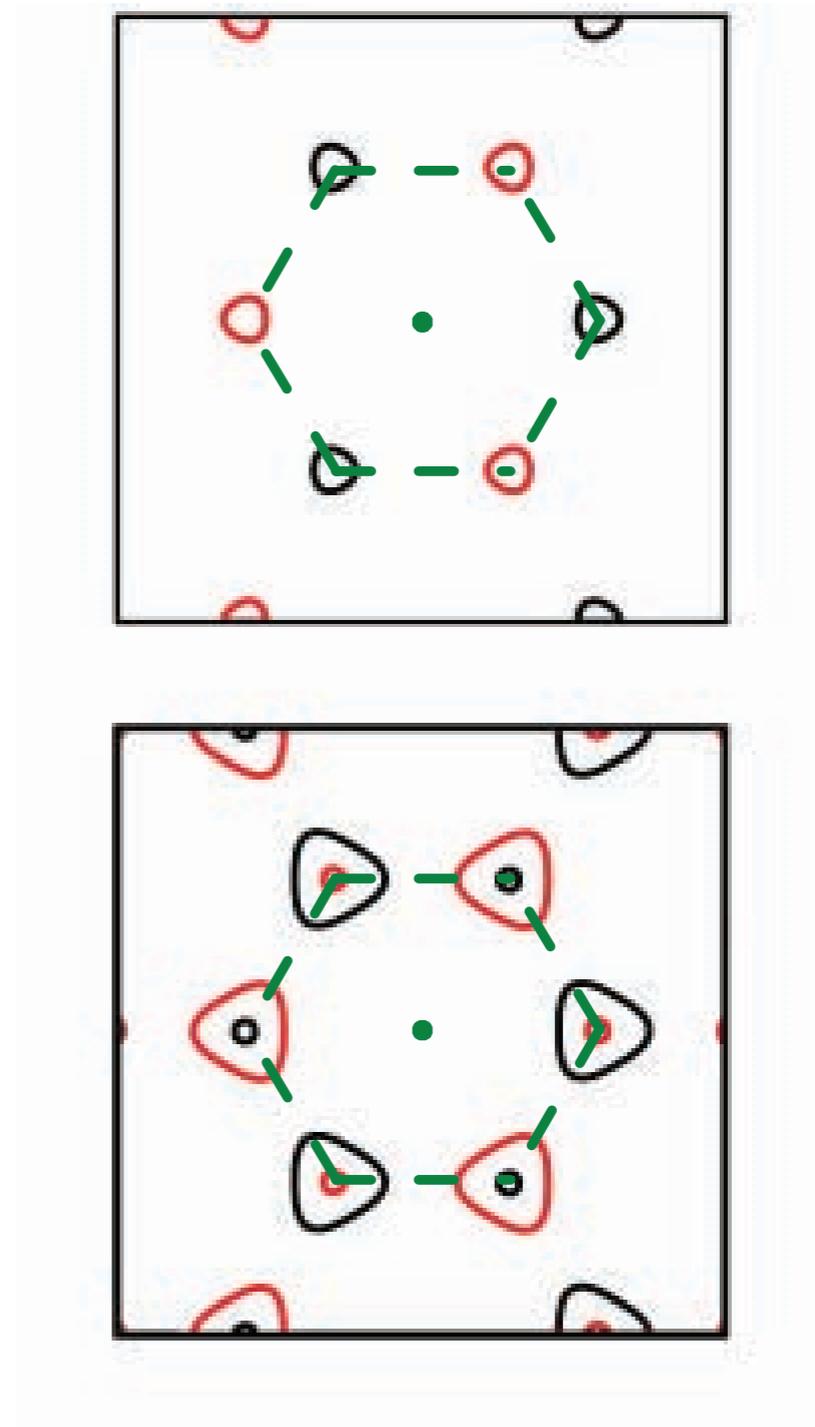
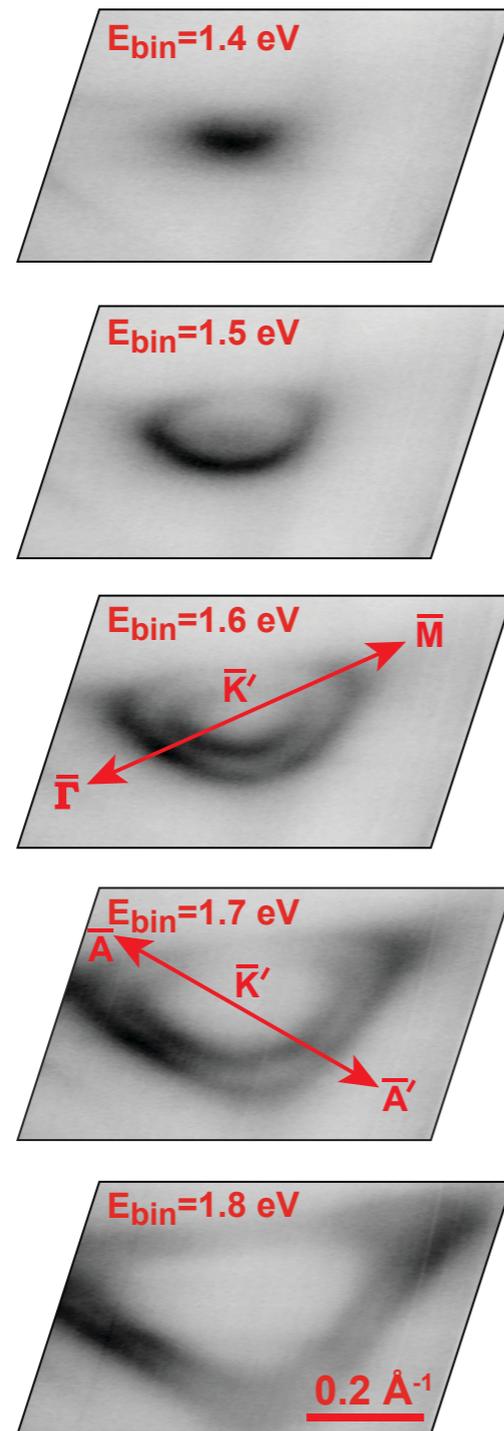


calc.: Z. Y. Zhu *et al.*, Phys. Rev. B **84**, 153402 (2012)



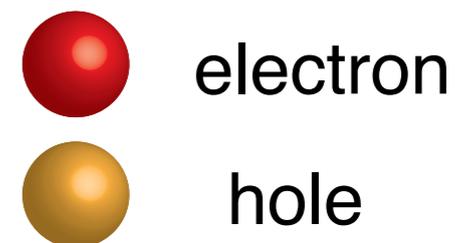
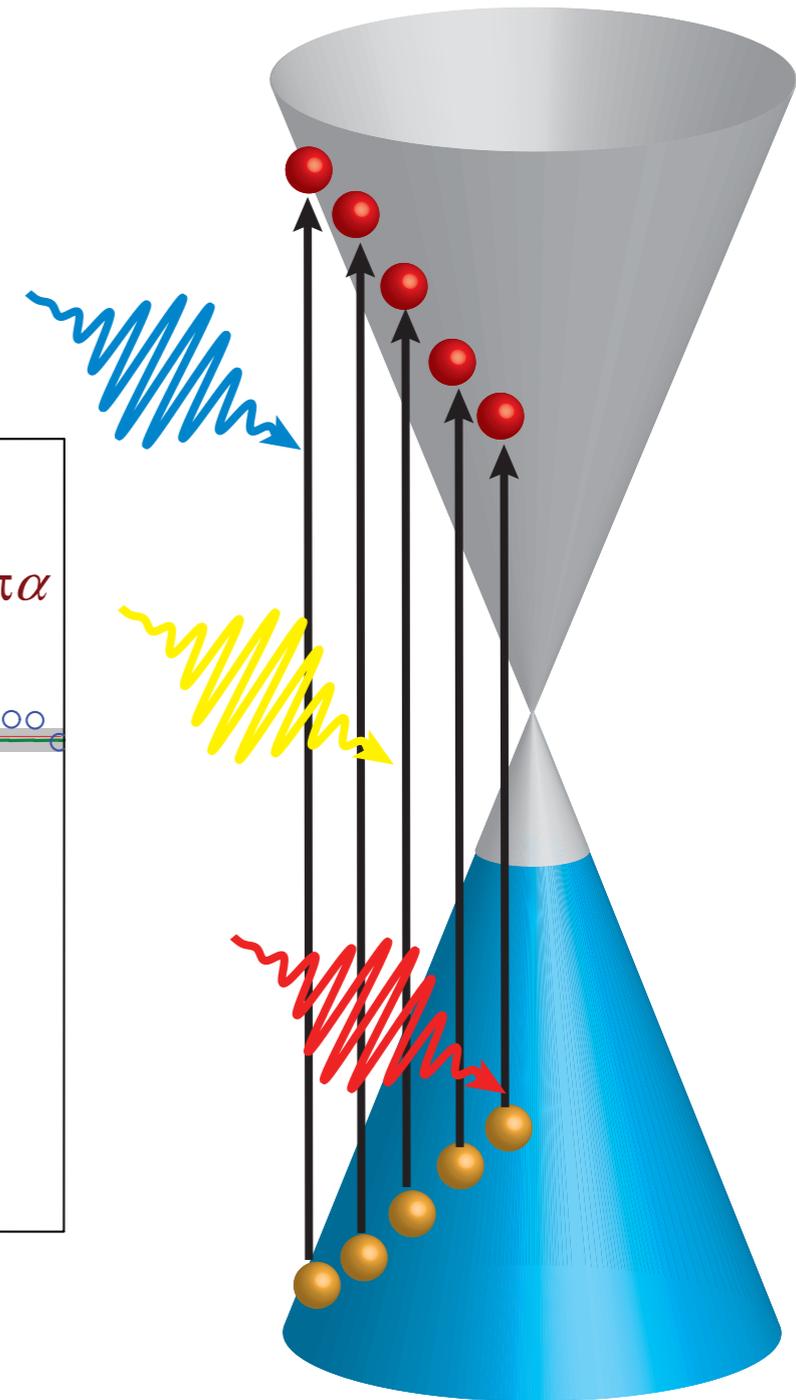
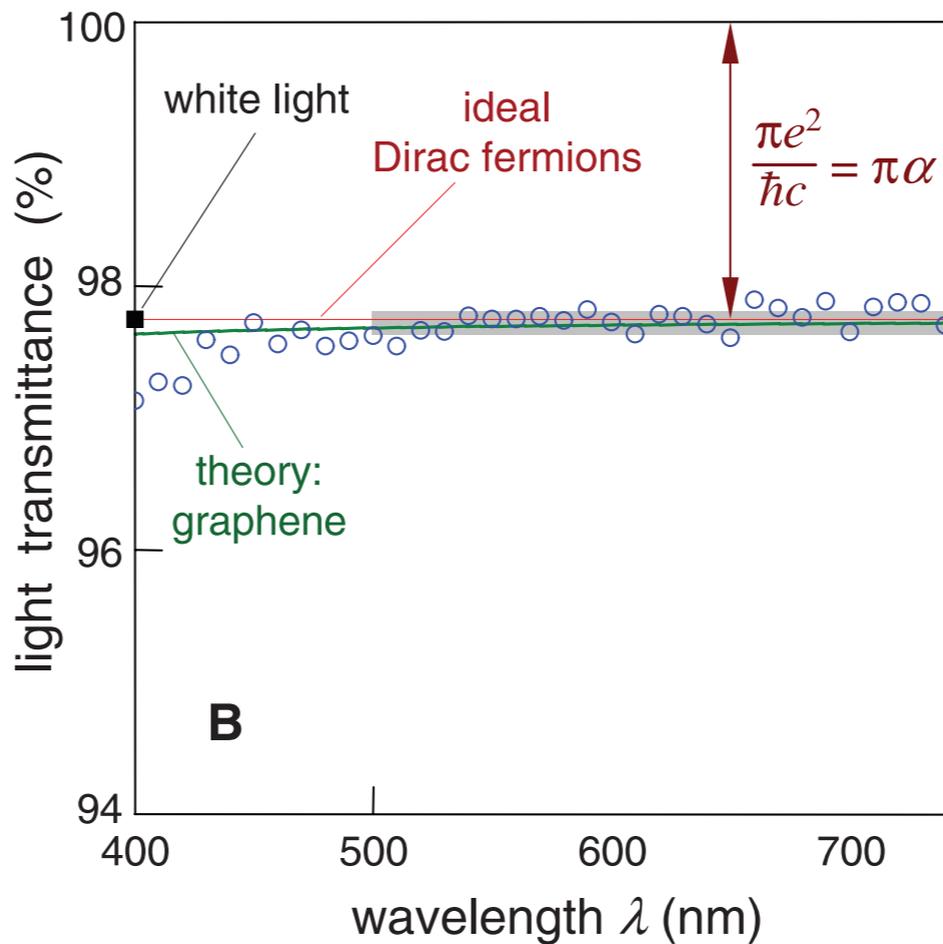
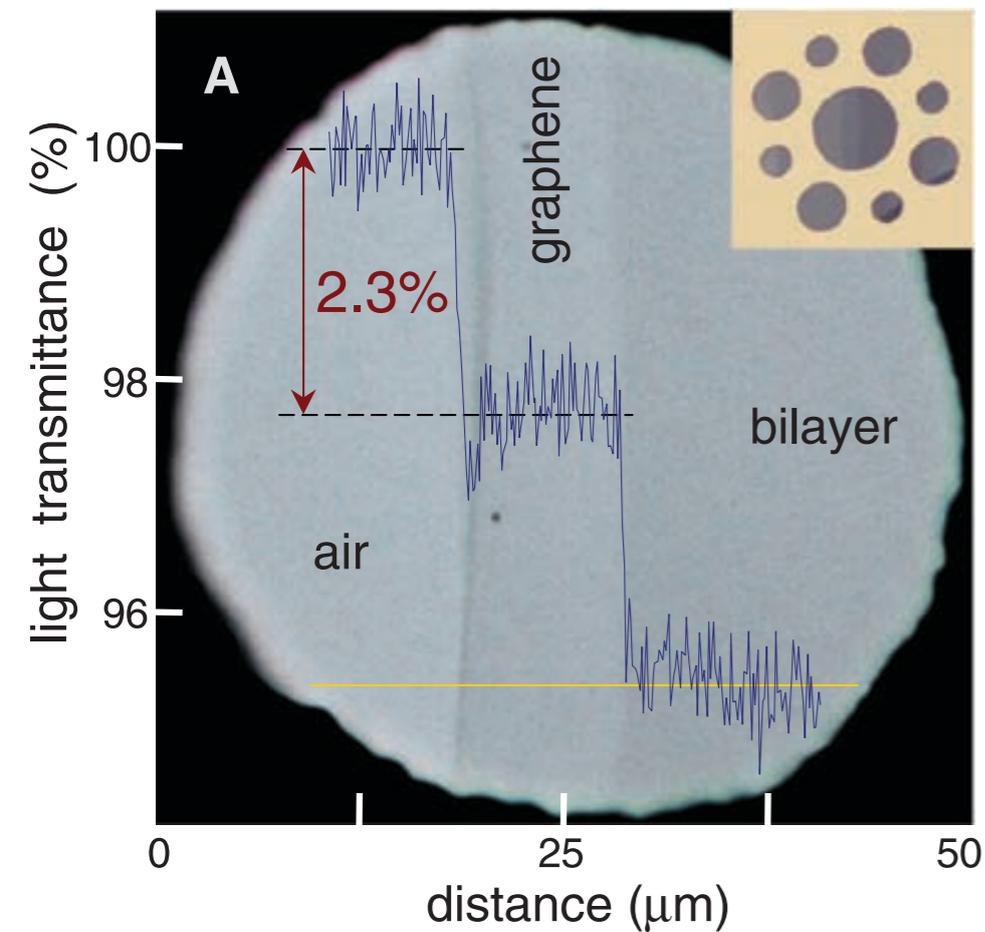
Wencan Jin *et al.*, PRL **111**, 106801 (2013)

spin-splitting compared to theory



- modifying the properties of epitaxial graphene
- spin splitting in WSe_2 and MoS_2
- **ultrafast carrier dynamics**

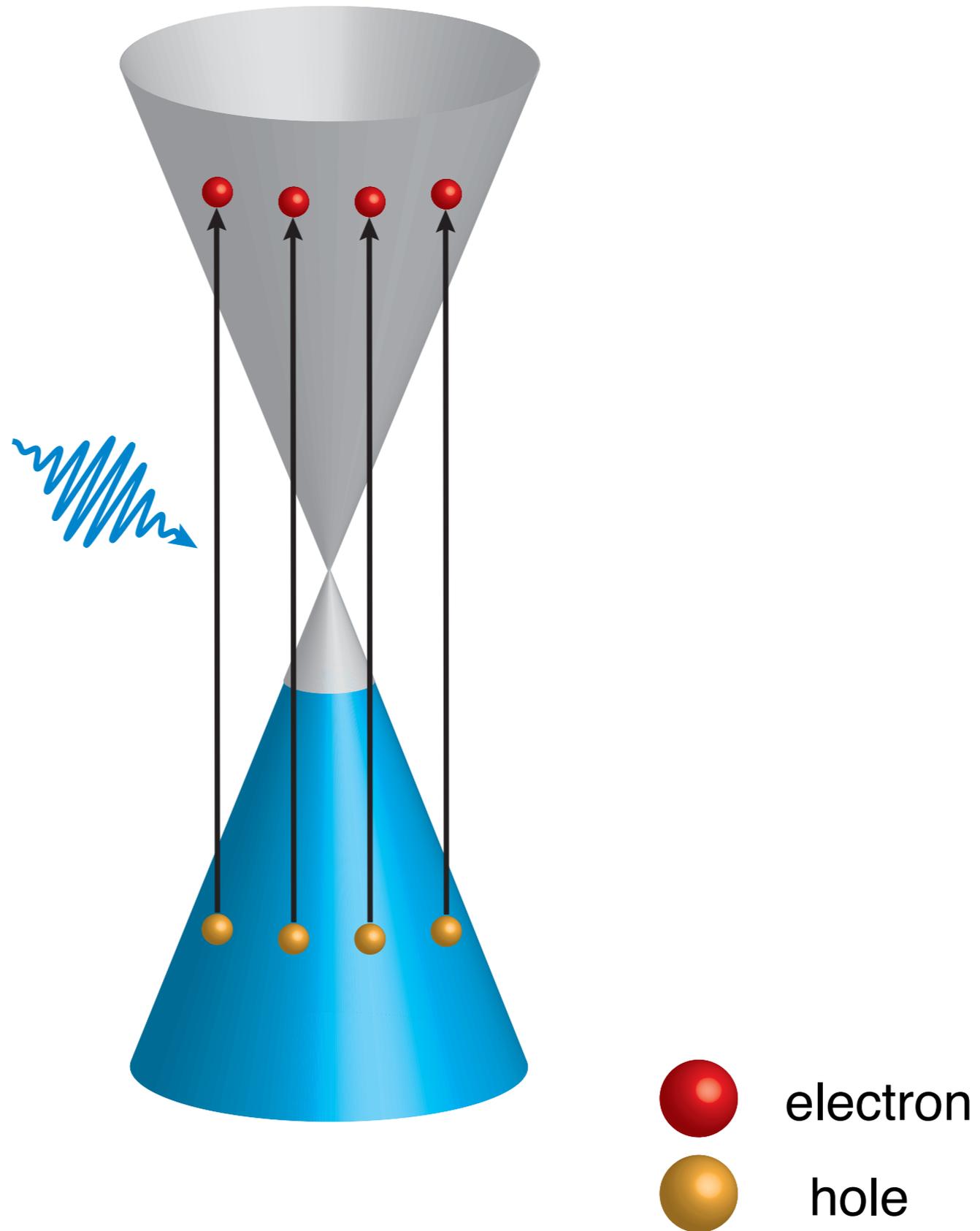
graphene appears very transparent...



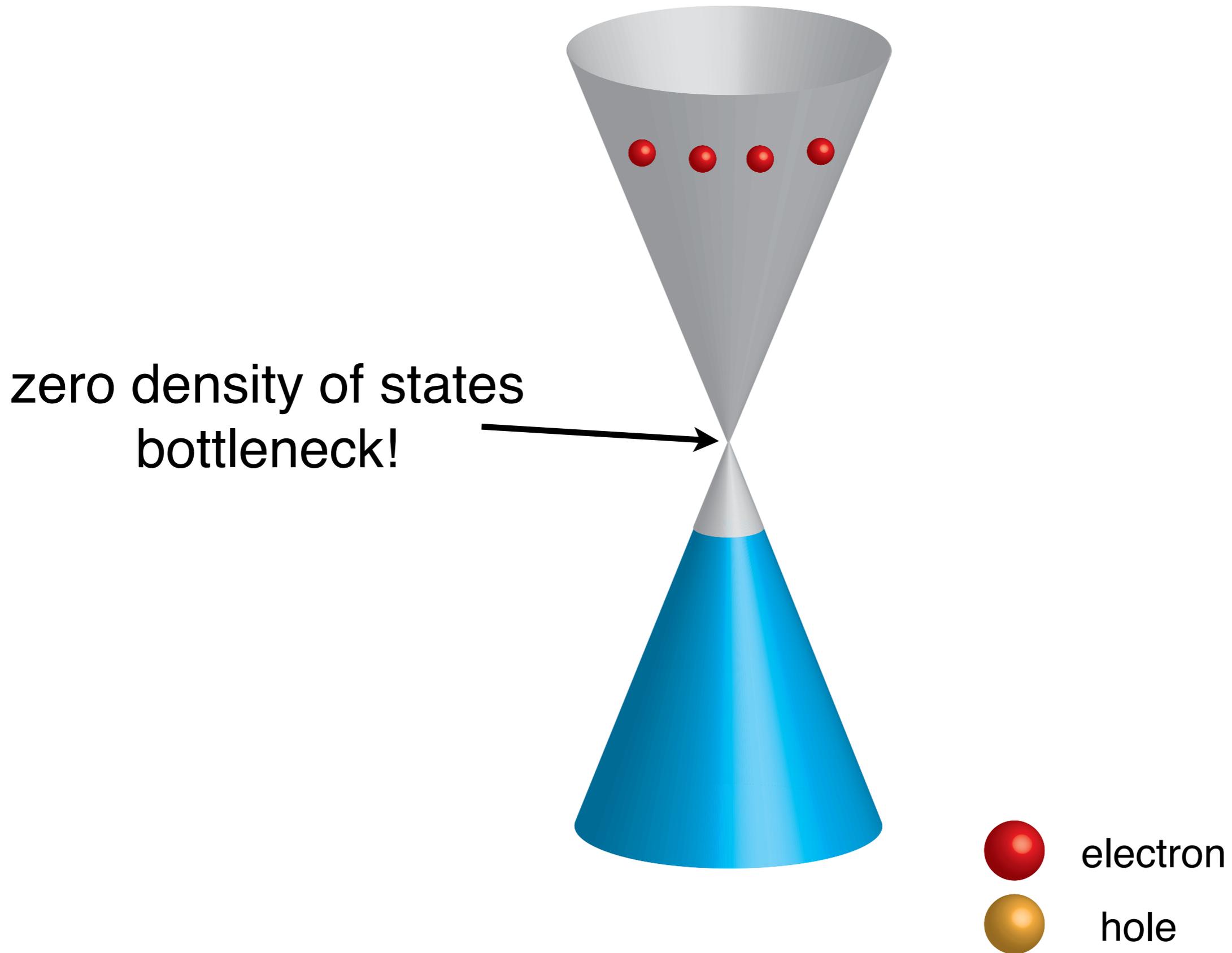
Nair *et al.*, Science **320**, 1308 (2008)
Mak *et al.*, PRL **101**, 196405 (2008)

what happens to the excited carriers?

$t = 0$ fs

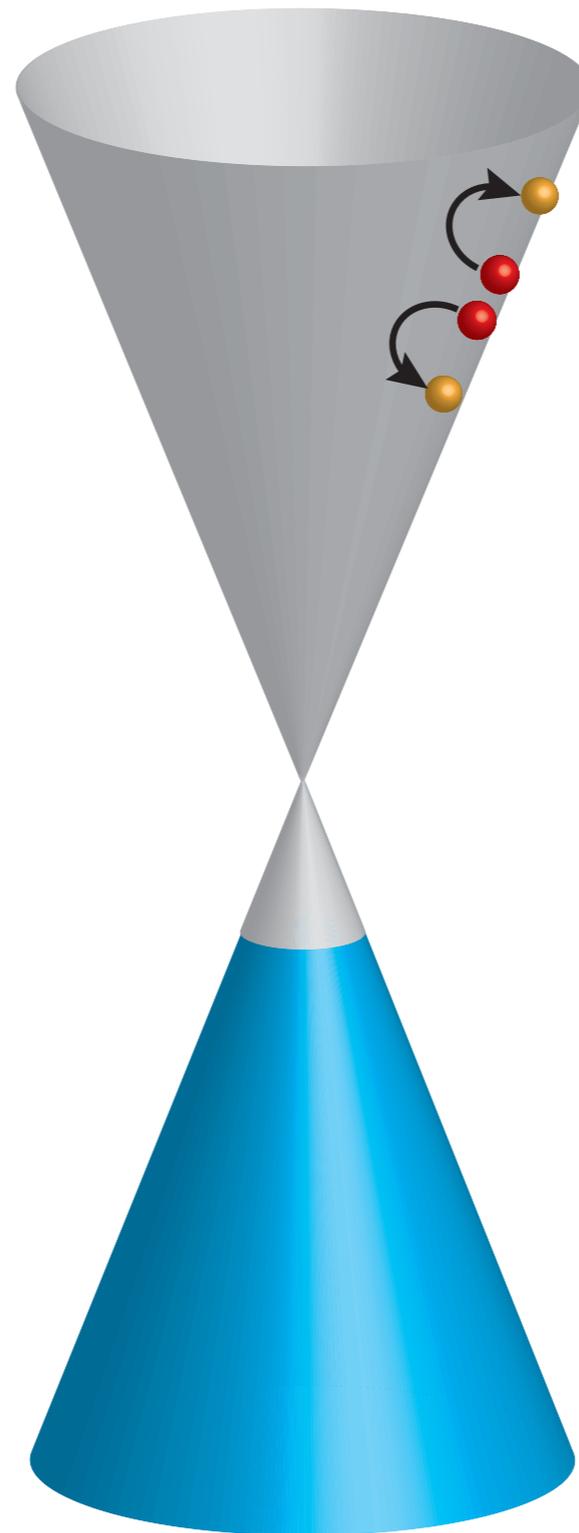


what happens to the excited carriers?



what happens to the excited carriers?

$t < 20 \text{ fs}$

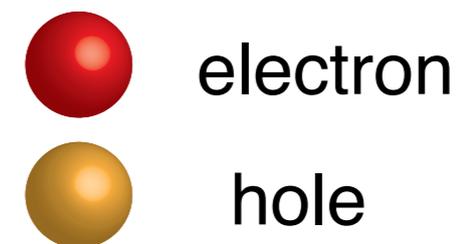
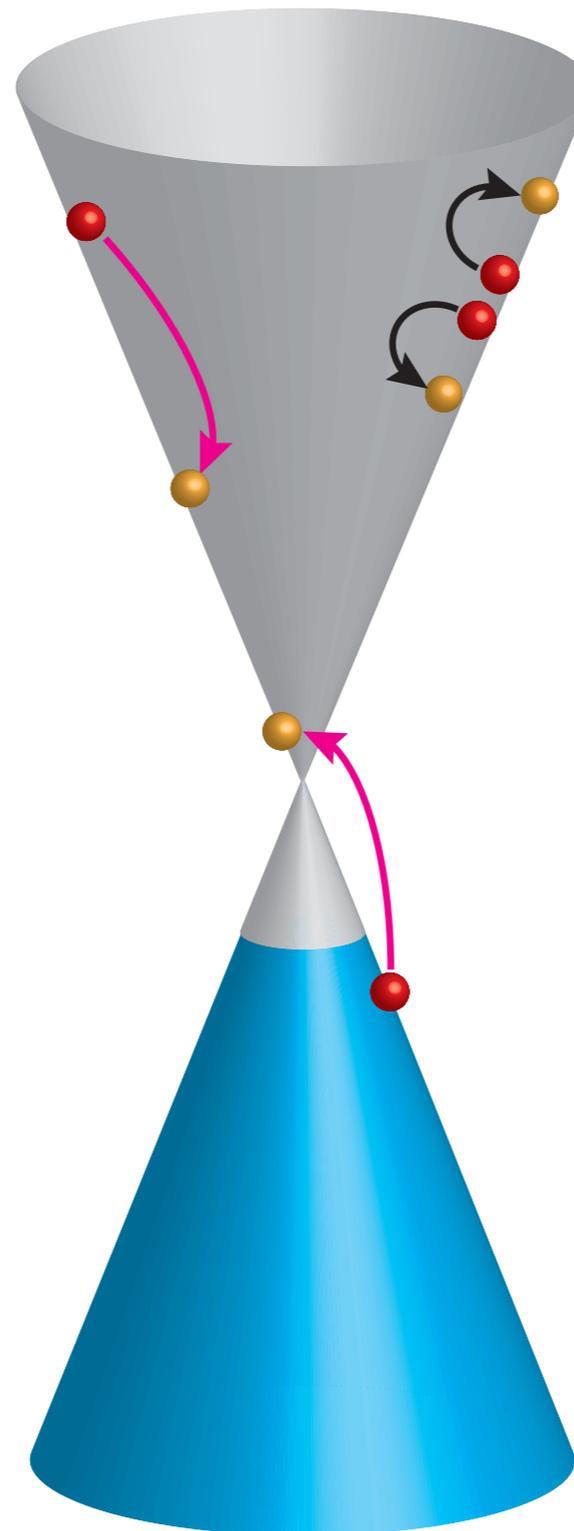


-  electron
-  hole

what happens to the excited carriers?

$t < 20$ fs

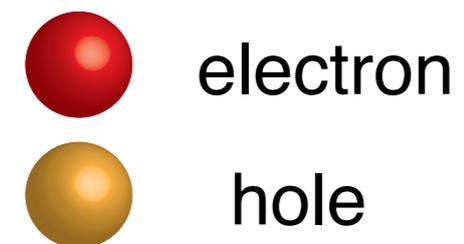
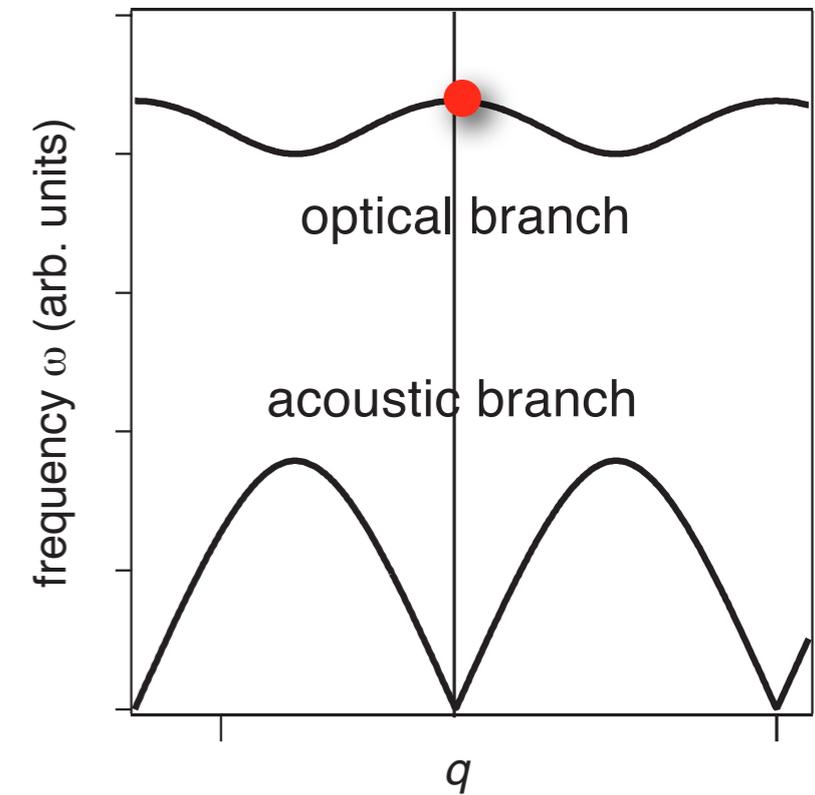
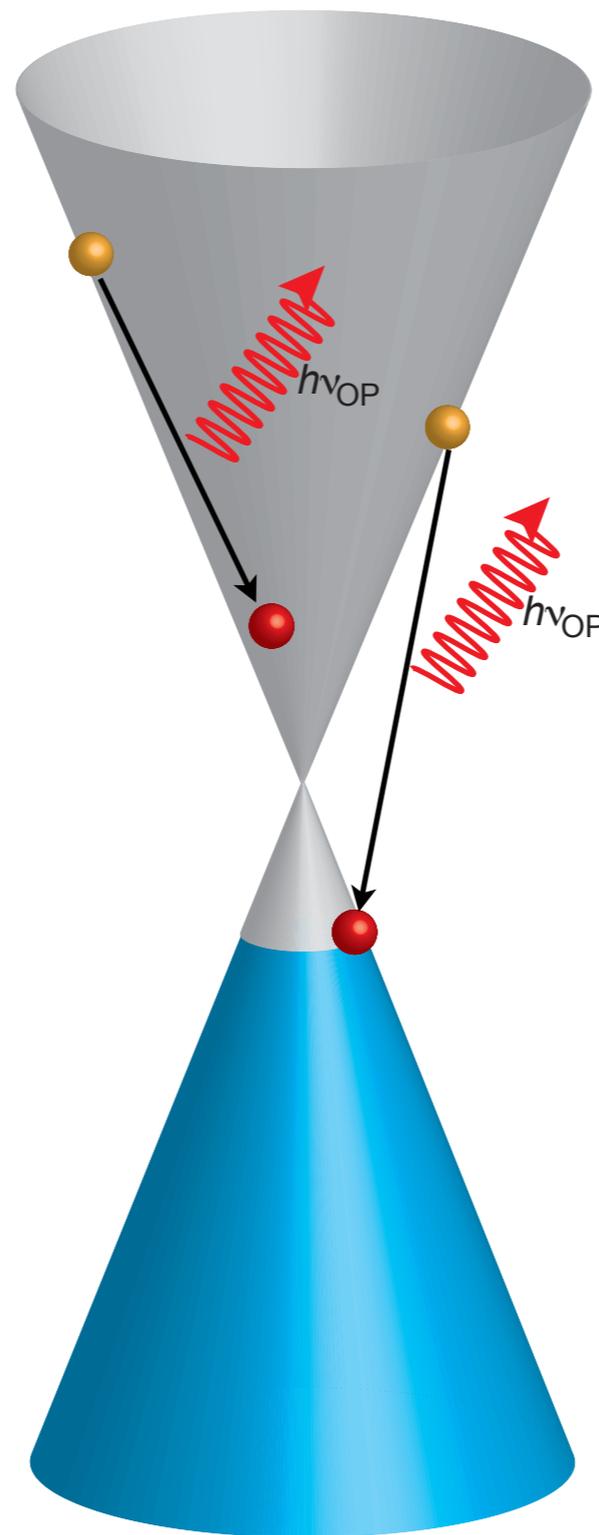
(after that hot
but thermal
distribution)



what happens to the excited carriers?

$20 \text{ fs} < t < 250 \text{ fs}$

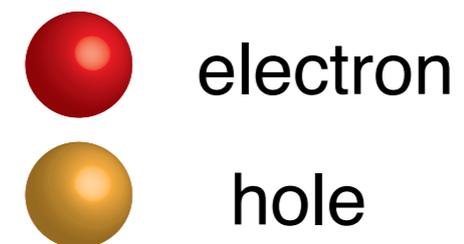
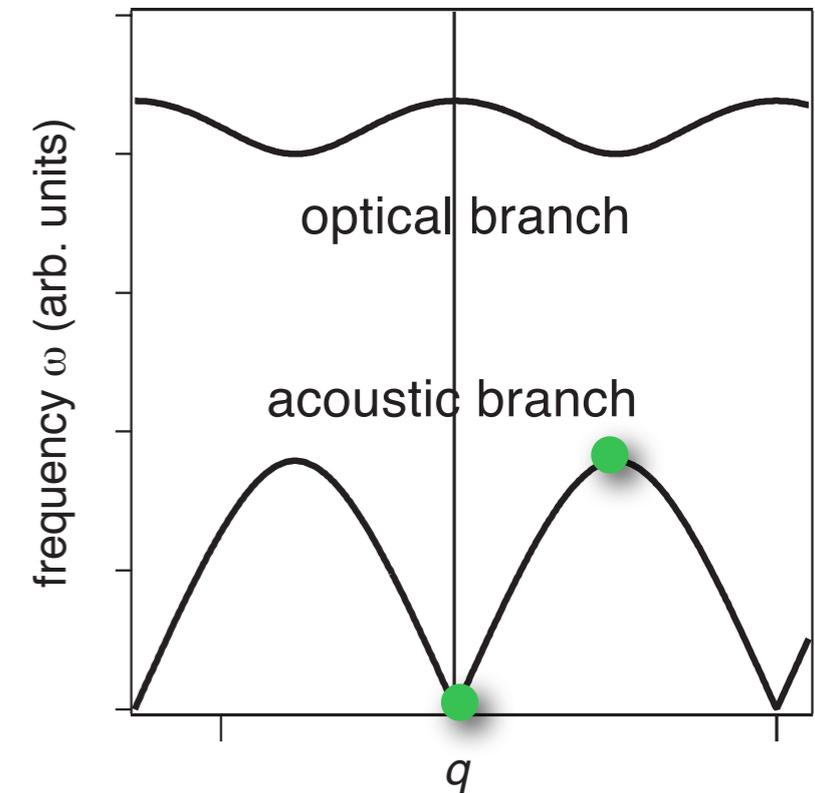
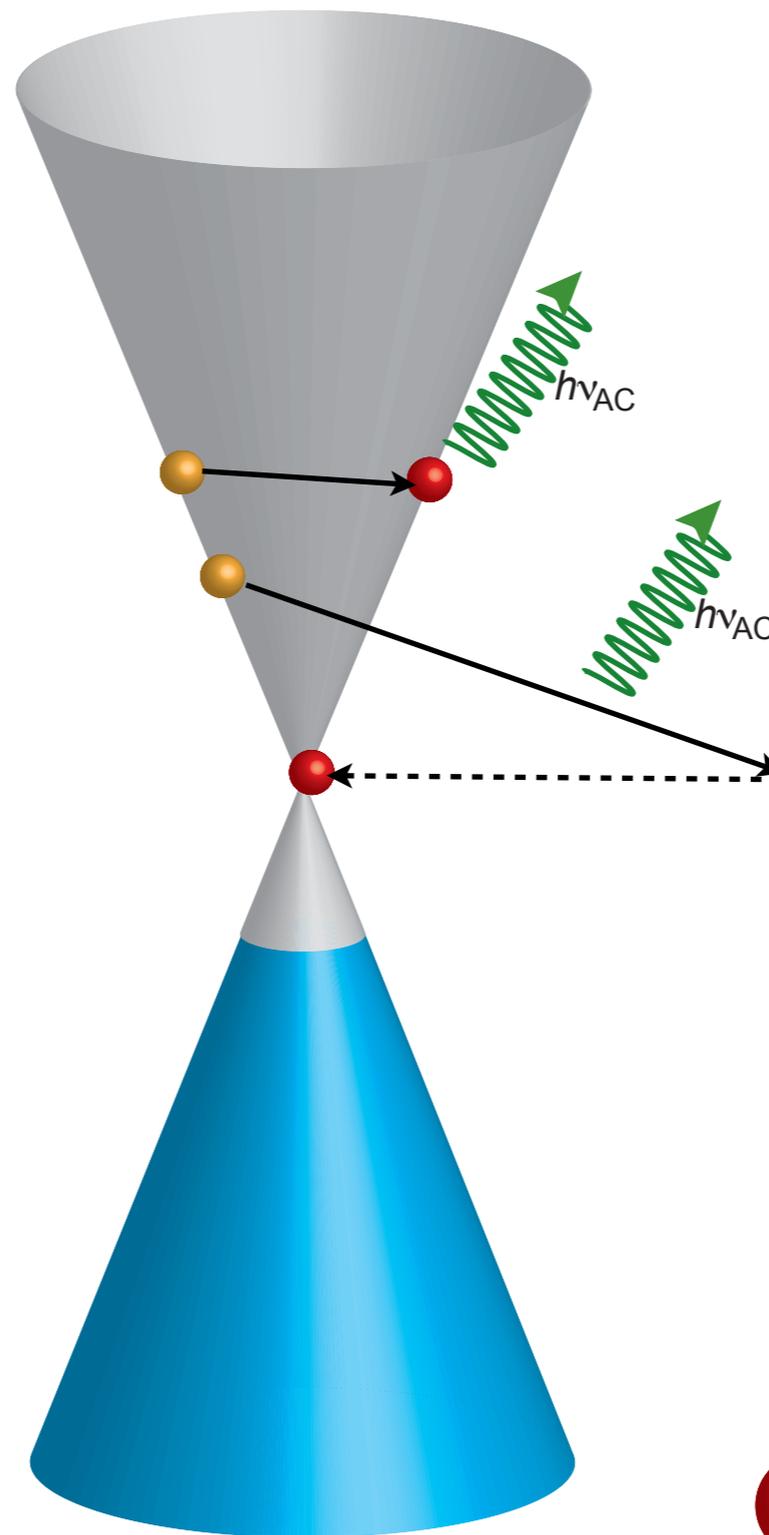
(after that hot
but thermal
distribution)



what happens to the excited carriers?

$t > 250$ fs

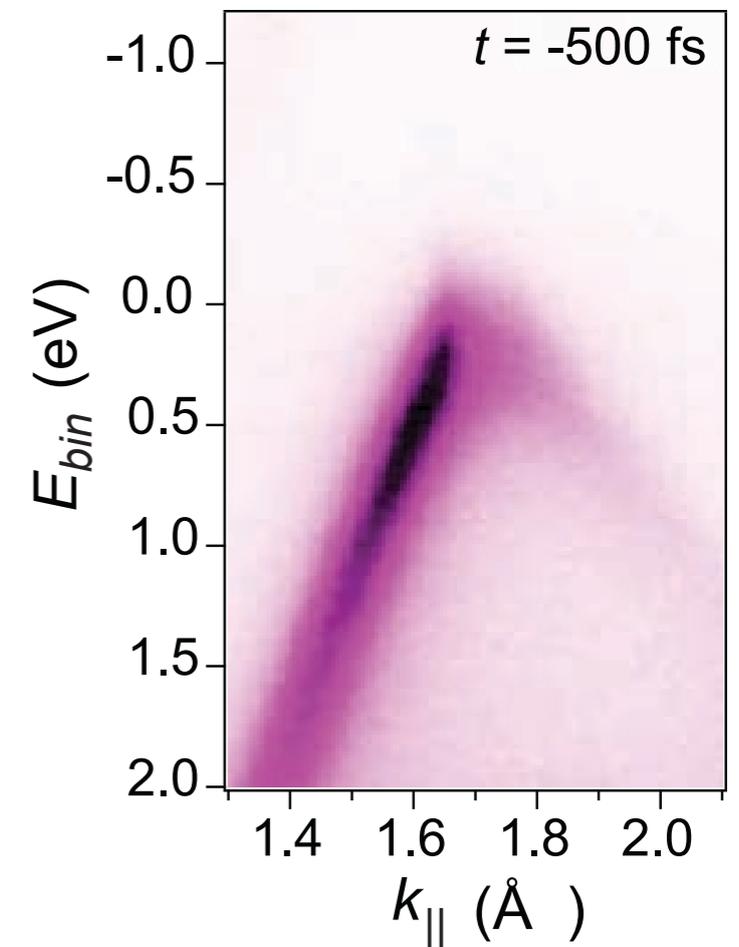
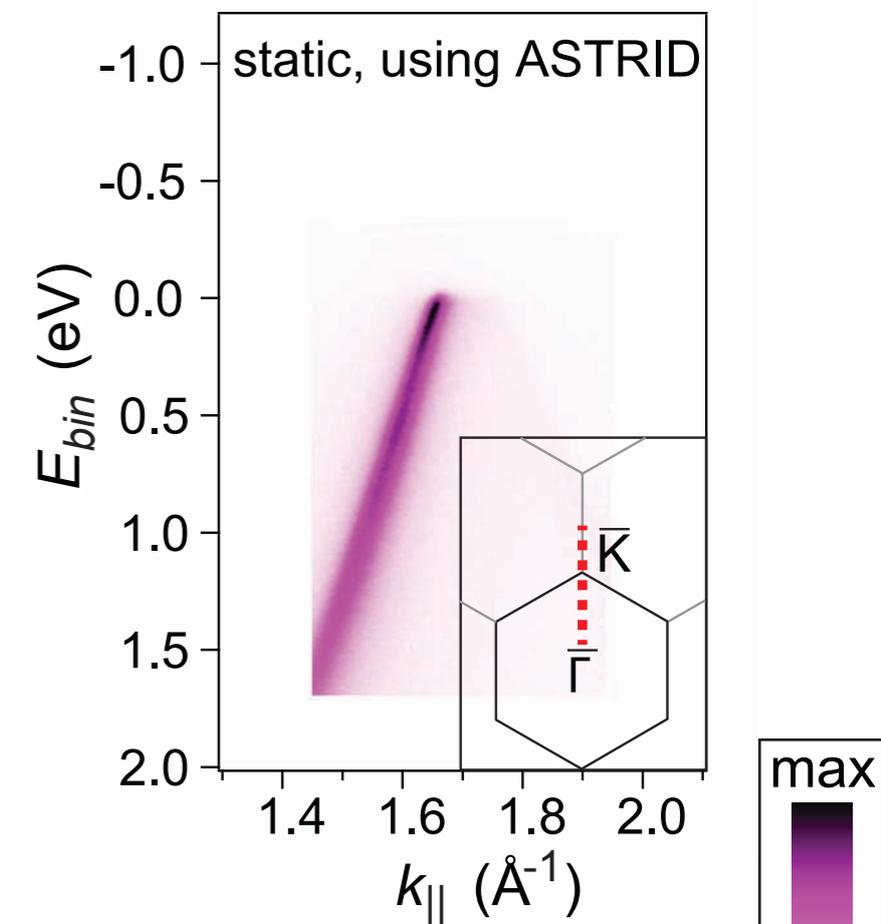
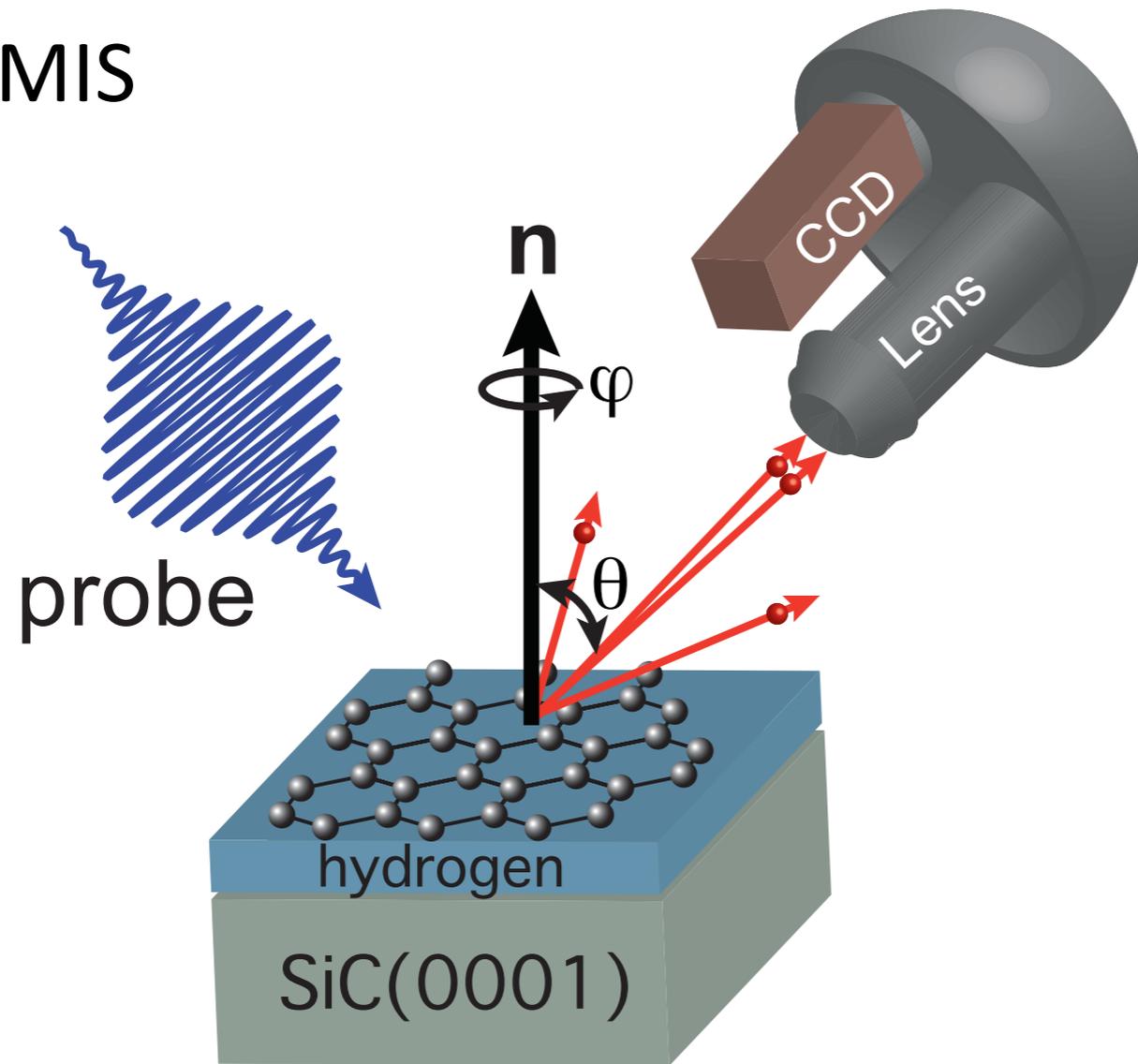
(after that hot but thermal distribution)



time-resolved ARPES



ARTEMIS

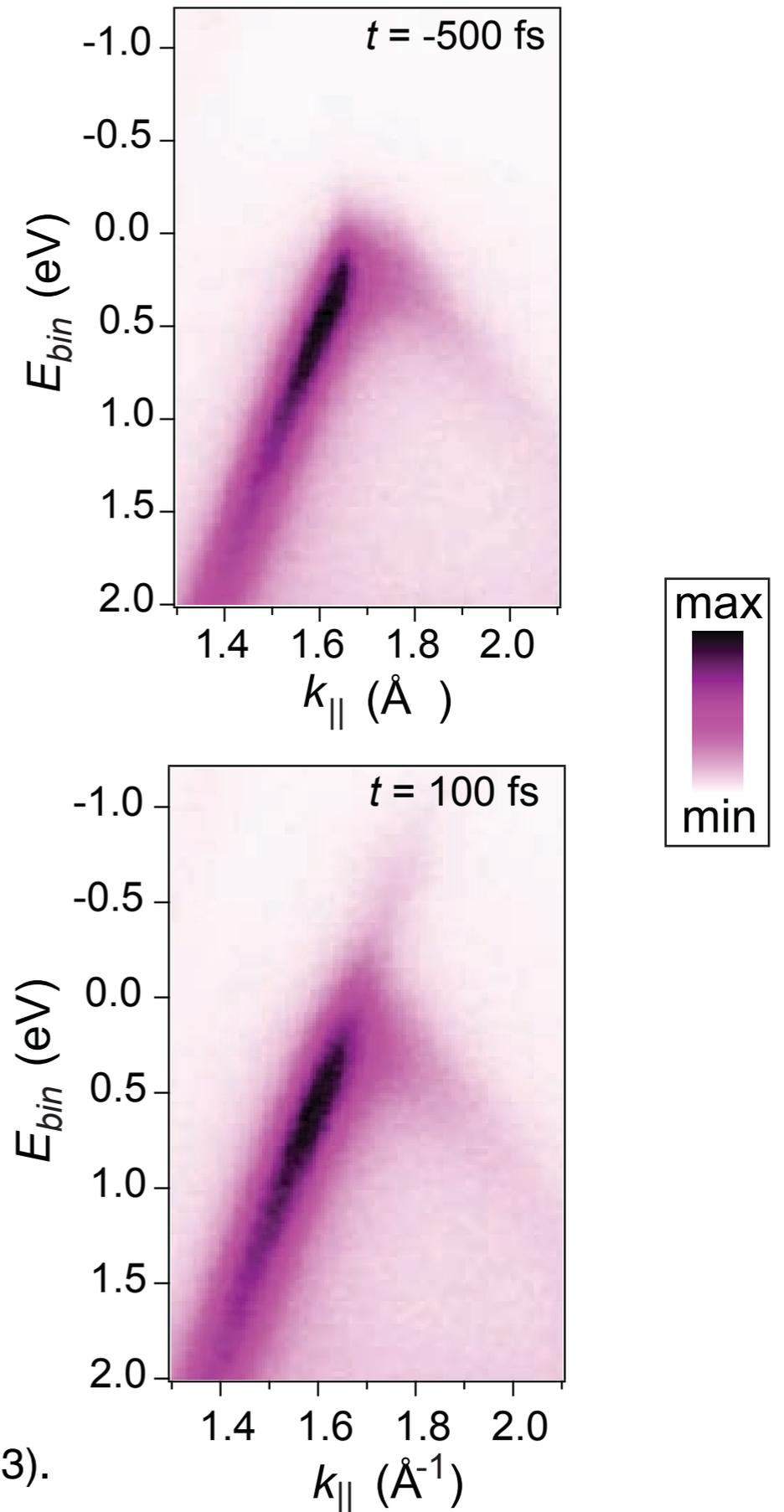
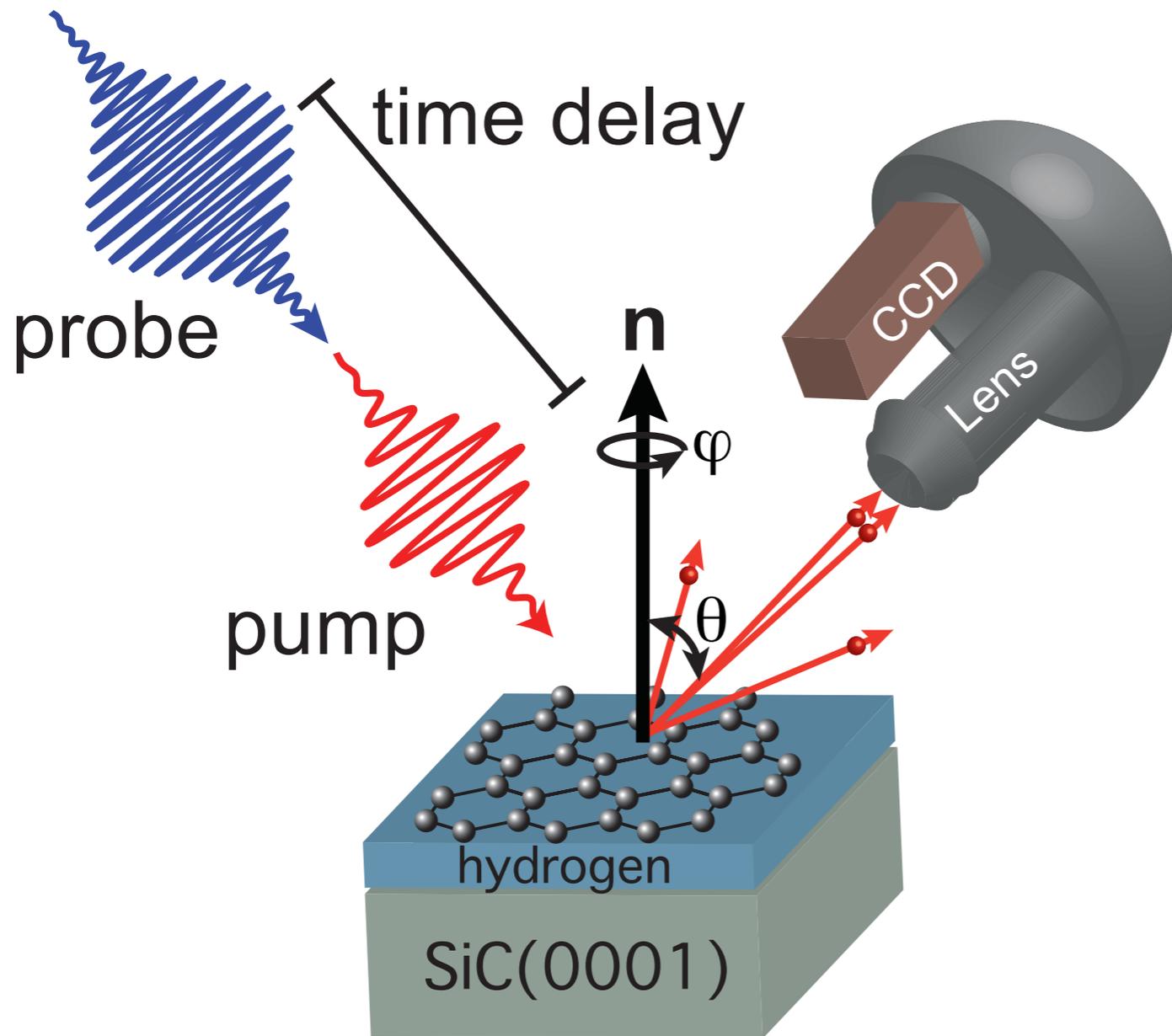


- Riedl *et al.*, PRL **103** 246804 (2009)
Speck *et al.*, APL **99** 122106 (2011)
Bostwick *et al.*, Science **328** 999 (2010)
Johannsen *et al.*, J. Phys.: Condens. Matter **25** 094001 (2013)

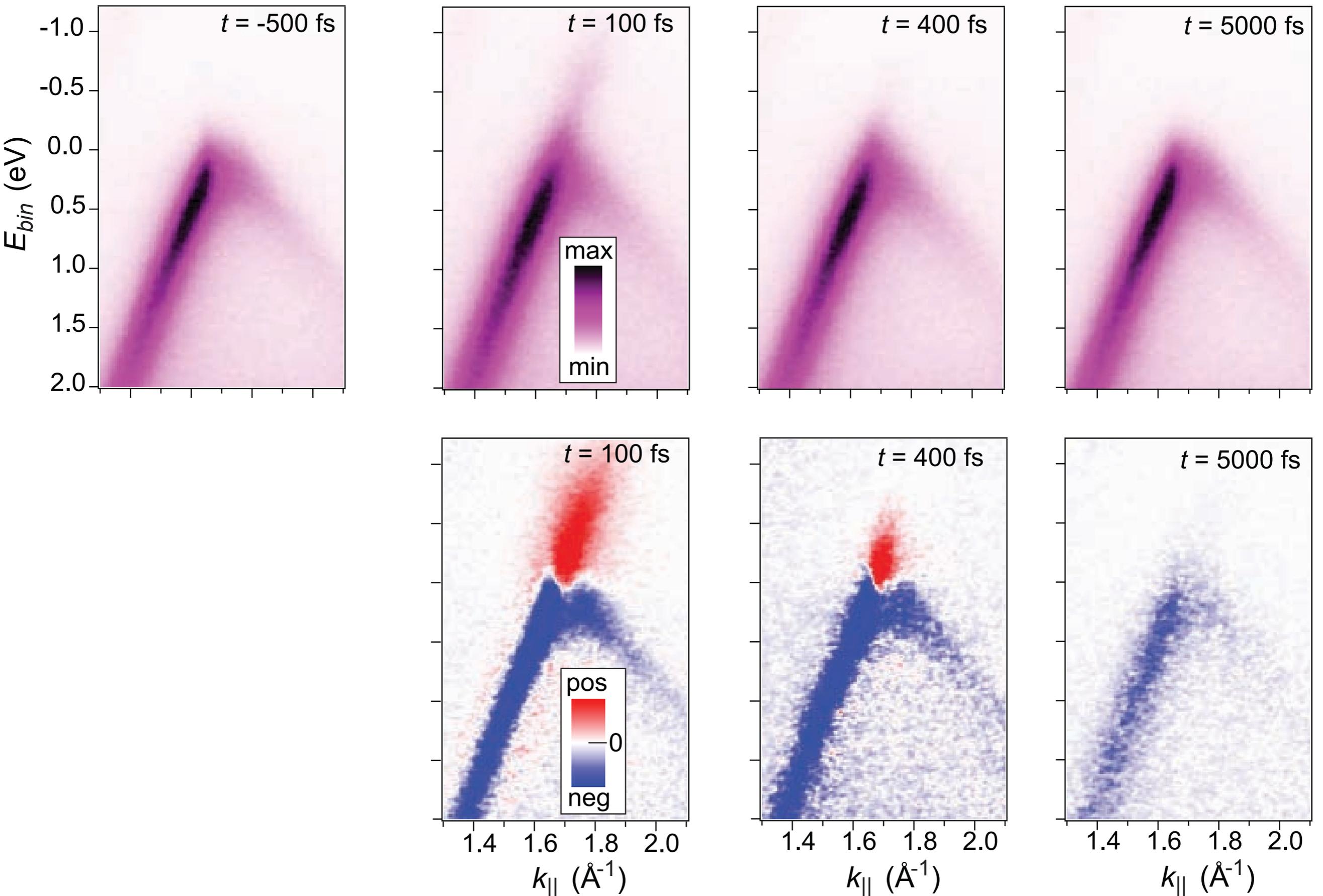
time-resolved ARPES



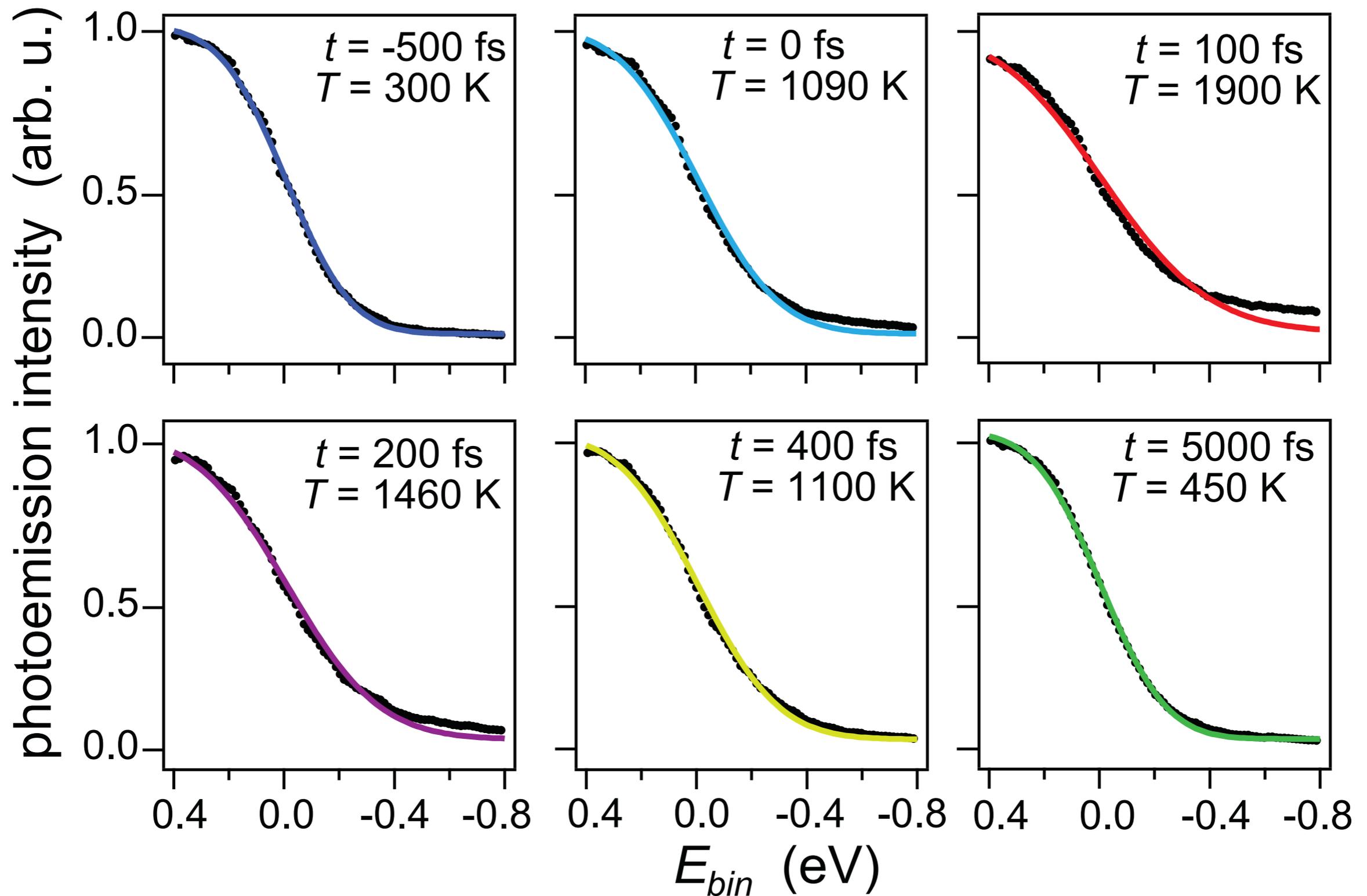
ARTEMIS



time-resolved ARPES view on Dirac cone



electronic temperature



three temperature model

Phenomenological system of coupled rate equations for T_e , T_p (modeled as Einstein mode) and T_l

Gaussian source term

Supercollision term

$$\frac{\partial T_e}{\partial t} = + \frac{S(t)}{\beta} - \frac{\pi \lambda_1 g(\mu(T_e)) \Omega_{Ein}^3 n_e - n_p}{\hbar C_e} - 9.62 \frac{\lambda_2 g(\mu(T_e)) k_B^3 T_e^3 - T_l^3}{\hbar k_{Fl} C_e}$$

$$- \pi \lambda_2 \hbar g(\mu(T_e)) k_F^2 v_s^2 k_B \frac{T_e - T_l}{C_e}$$

Optical phonon term

$$\frac{\partial T_p}{\partial t} = \frac{C_e}{C_p} \frac{\pi \lambda_1 g(\mu(T_e)) \Omega_{Ein}^3 n_e - n_p}{\hbar C_e}$$

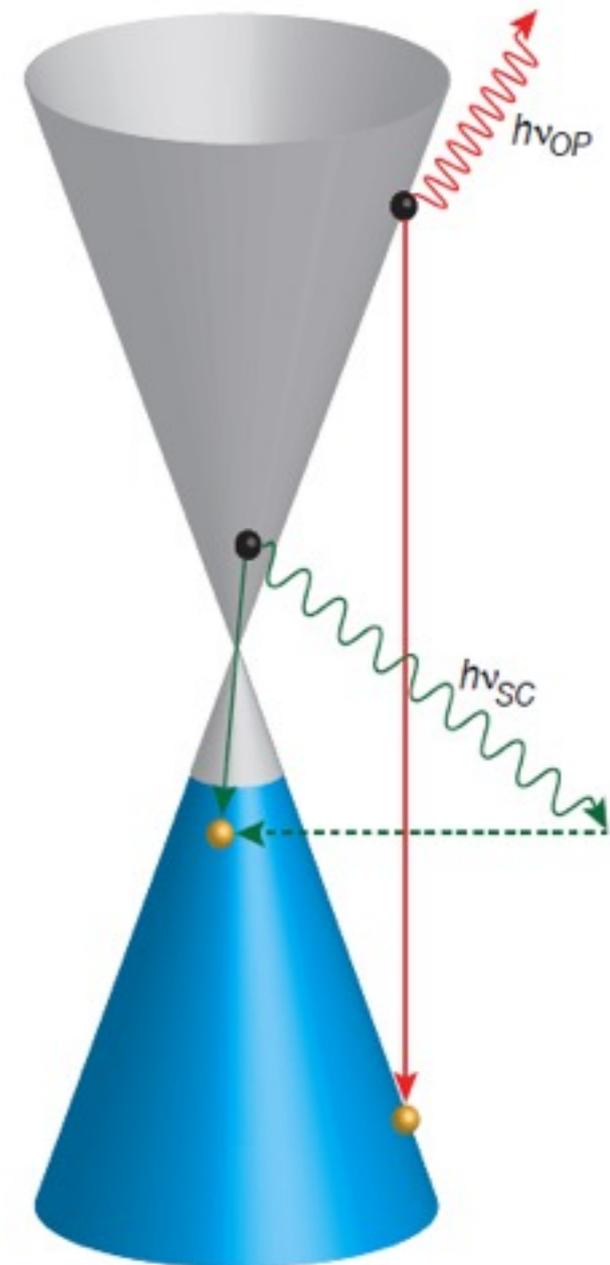
Direct acoustic phonon term

$$\frac{\partial T_l}{\partial t} = \frac{C_e}{C_l} \left(9.62 \frac{\lambda_2 g(\mu(T_e)) k_B^3 T_e^3 - T_l^3}{\hbar k_{Fl} C_e} + \pi \lambda_2 \hbar g(\mu(T_e)) k_F^2 v_s^2 k_B \frac{T_e - T_l}{C_e} \right)$$

Supercollision term

Supercollision term:
Song *et al.*, PRL **109** 106602 (2012)

Direct term:
Bistritzer *et al.*, PRL **102** 206410 (2009)



three temperature model

Phenomenological system of coupled rate equations for T_e , T_p (modeled as Einstein mode) and T_l

$$\frac{\partial T_e}{\partial t} = + \frac{S(t)}{\beta} - \frac{\pi \lambda_1 g(\mu(T_e)) \Omega_{Ein}^3 n_e - n_p}{\hbar C_e} - 9.62 \frac{\lambda_2 g(\mu(T_e)) k_B^3 T_e^3 - T_l^3}{\hbar k_{Fl} C_e} - \pi \lambda_2 \hbar g(\mu(T_e)) k_F^2 v_s^2 k_B \frac{T_e - T_l}{C_e}$$

$$\frac{\partial T_p}{\partial t} = \frac{C_e}{C_p} \frac{\pi \lambda_1 g(\mu(T_e)) \Omega_{Ein}^3 n_e - n_p}{\hbar C_e}$$

$$\frac{\partial T_l}{\partial t} = \frac{C_e}{C_l} \left(9.62 \frac{\lambda_2 g(\mu(T_e)) k_B^3 T_e^3 - T_l^3}{\hbar k_{Fl} C_e} + \pi \lambda_2 \hbar g(\mu(T_e)) k_F^2 v_s^2 k_B \frac{T_e - T_l}{C_e} \right)$$

$k_{Fl} \approx 1.5$ (from static ARPES)

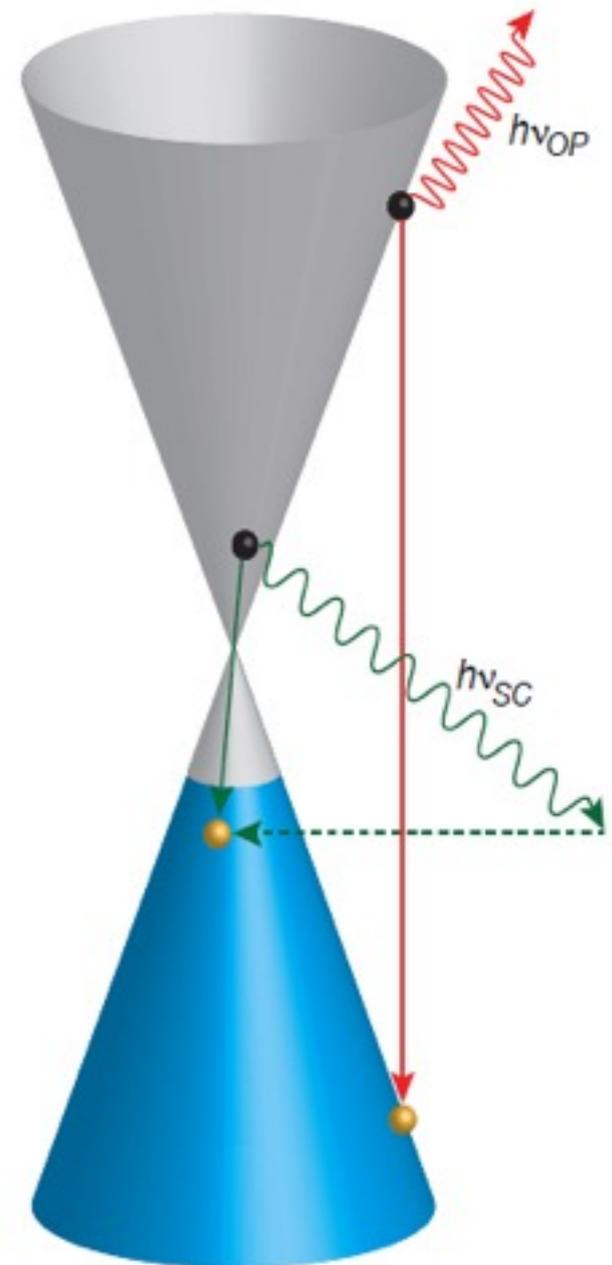
$\Omega_{Ein} = 200$ meV

$g(\mu)$: Density of states at the T_e -dependent chemical potential

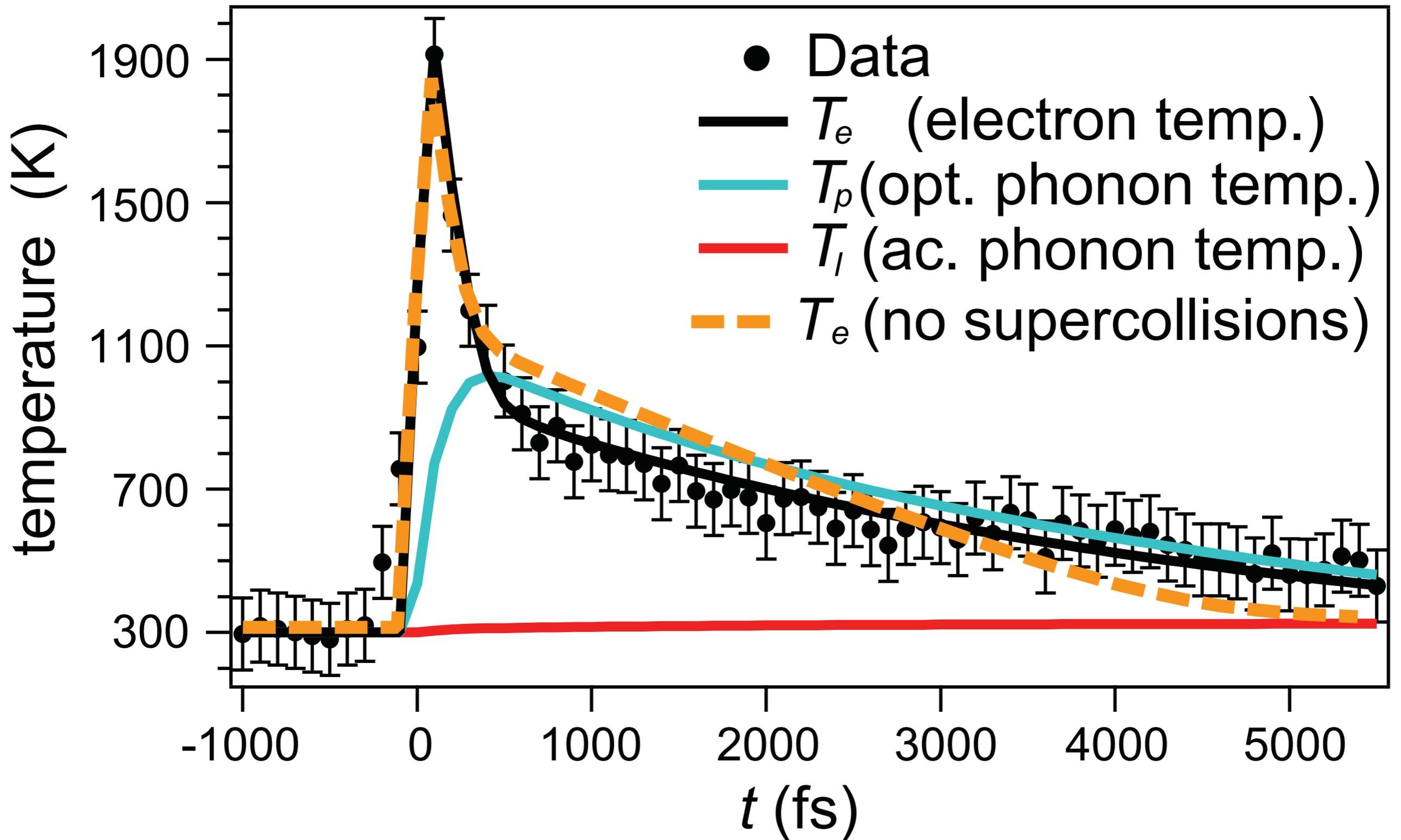
$v_s = 20000$ m/s (sound velocity in graphene)

C_e, C_p, C_l are heat capacities of each subsystem

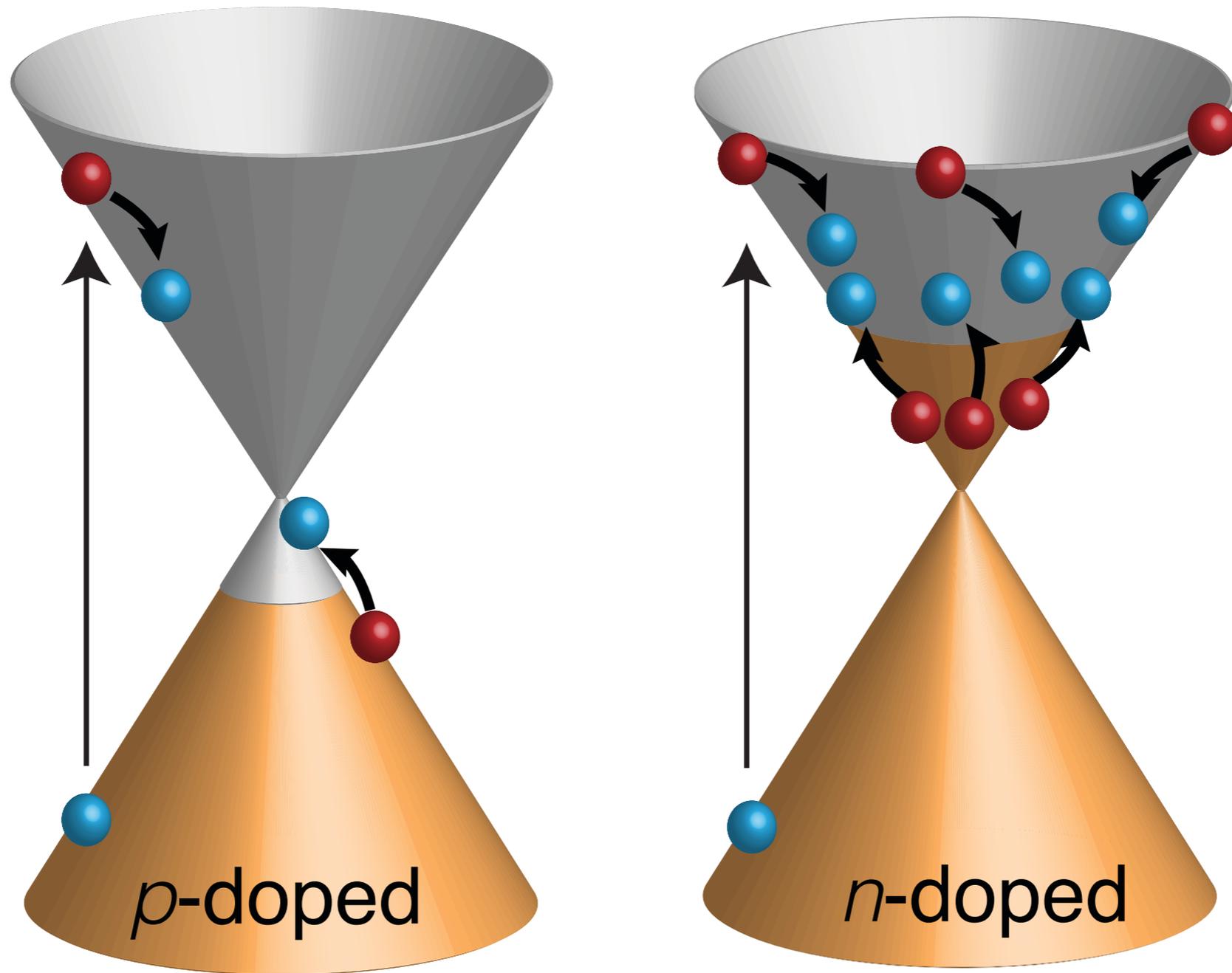
Three fit parameters: $\beta, \lambda_1, \lambda_2$



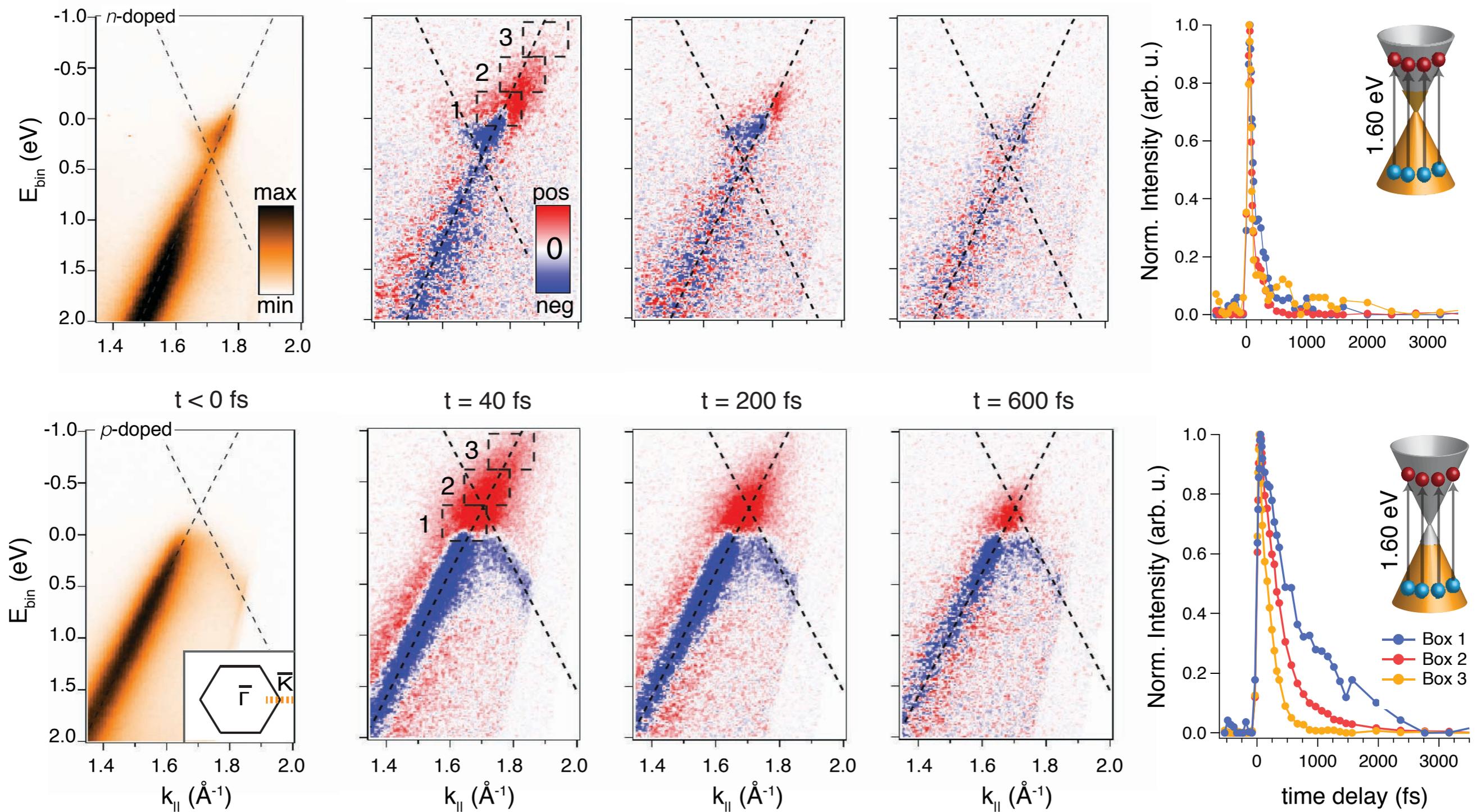
electronic temperature



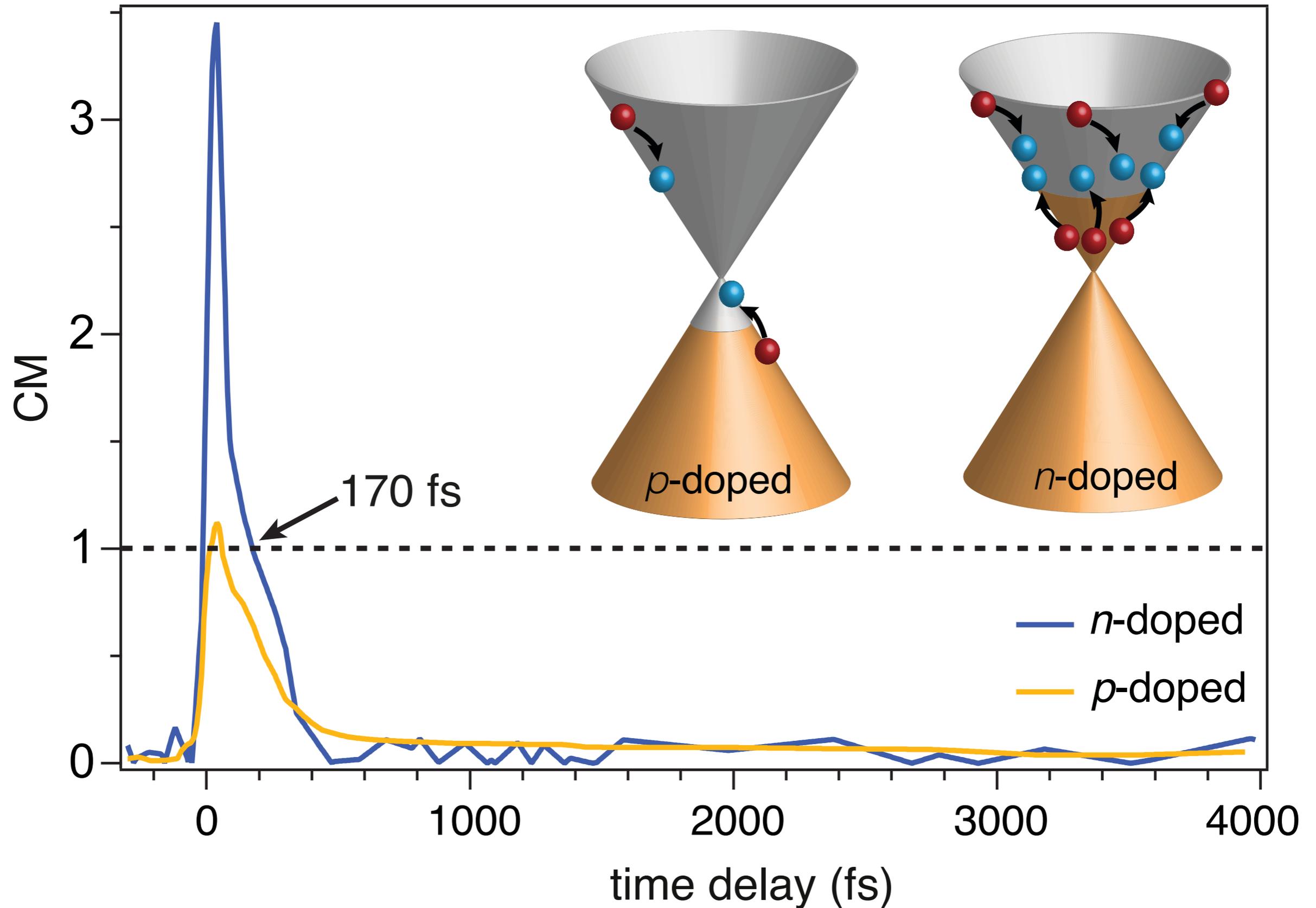
p-doped vs n-doped graphene



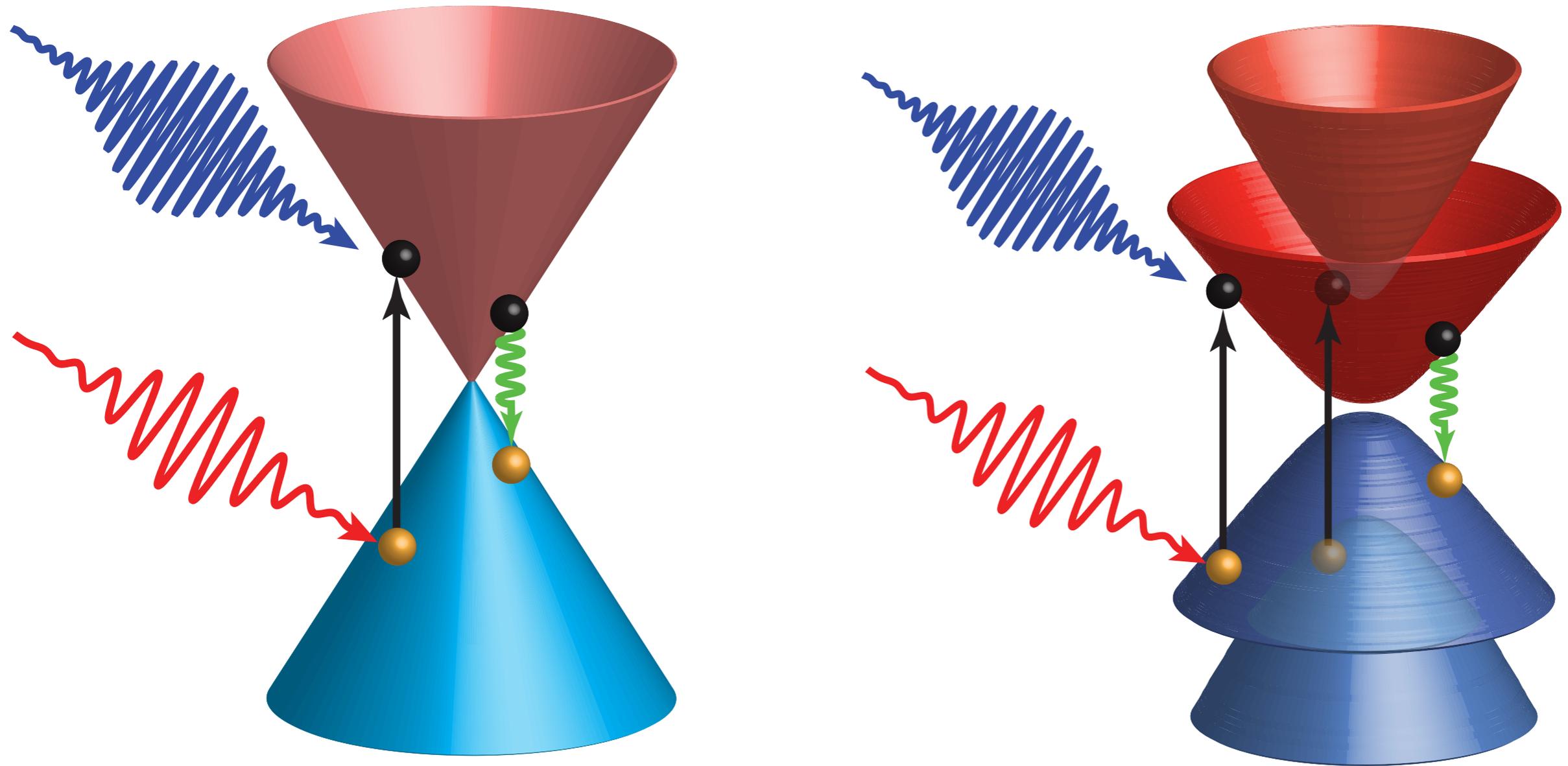
p-doped vs n-doped graphene

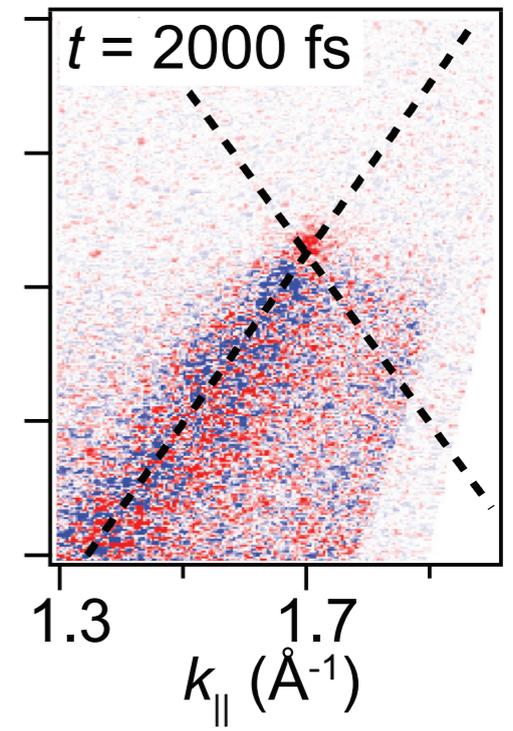
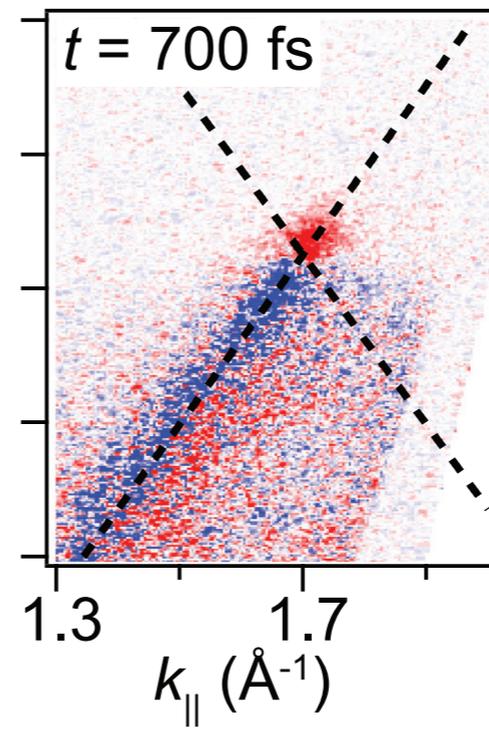
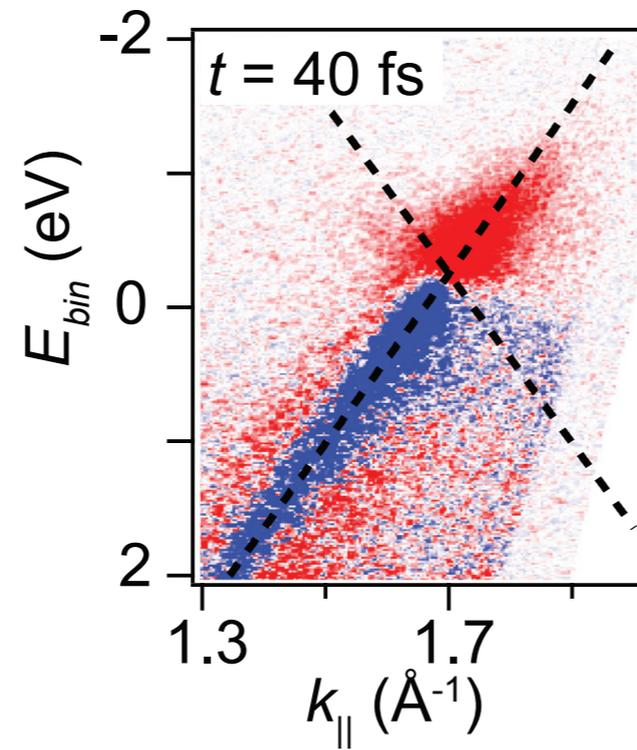
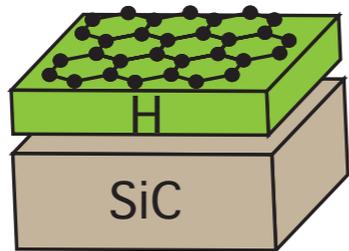
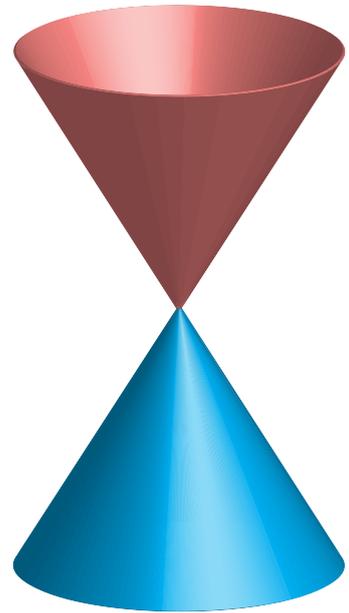
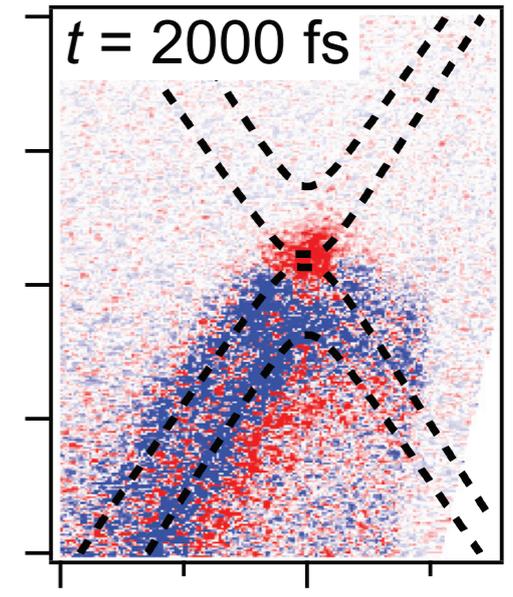
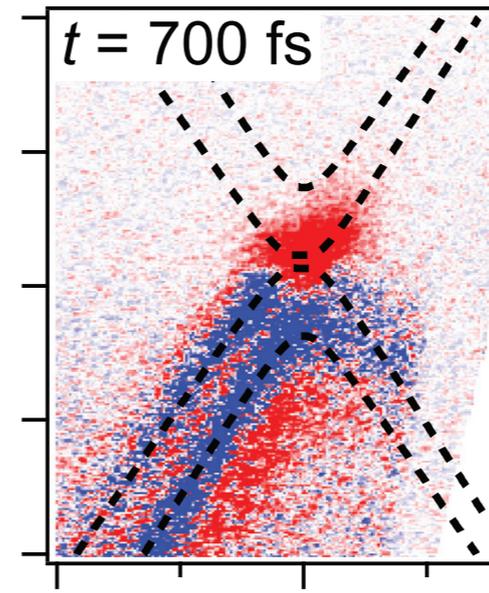
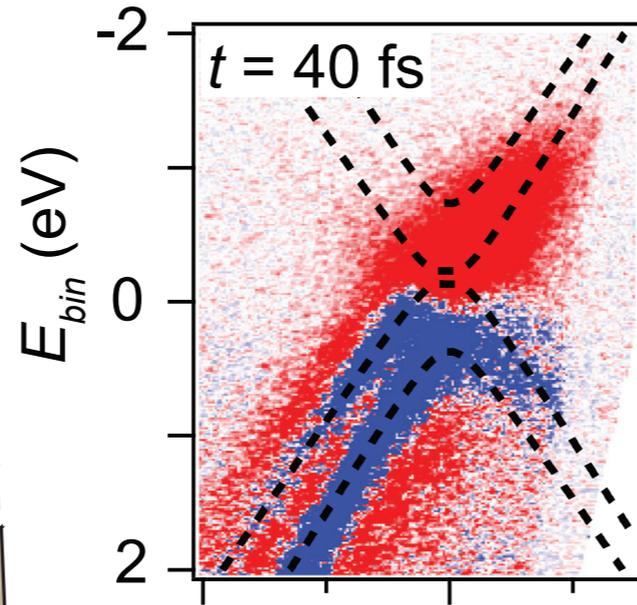
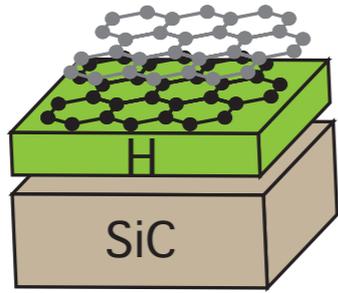
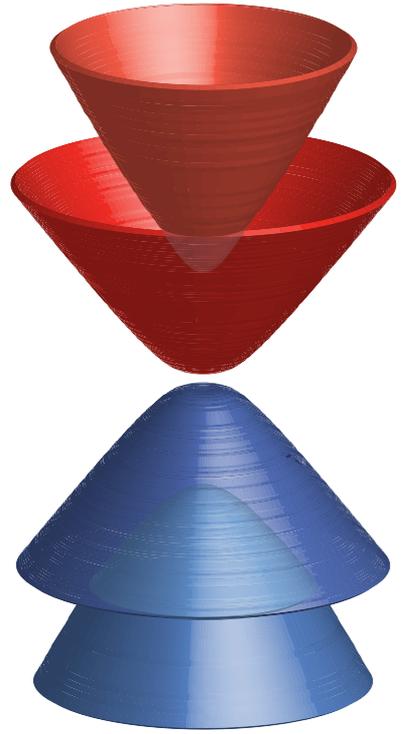


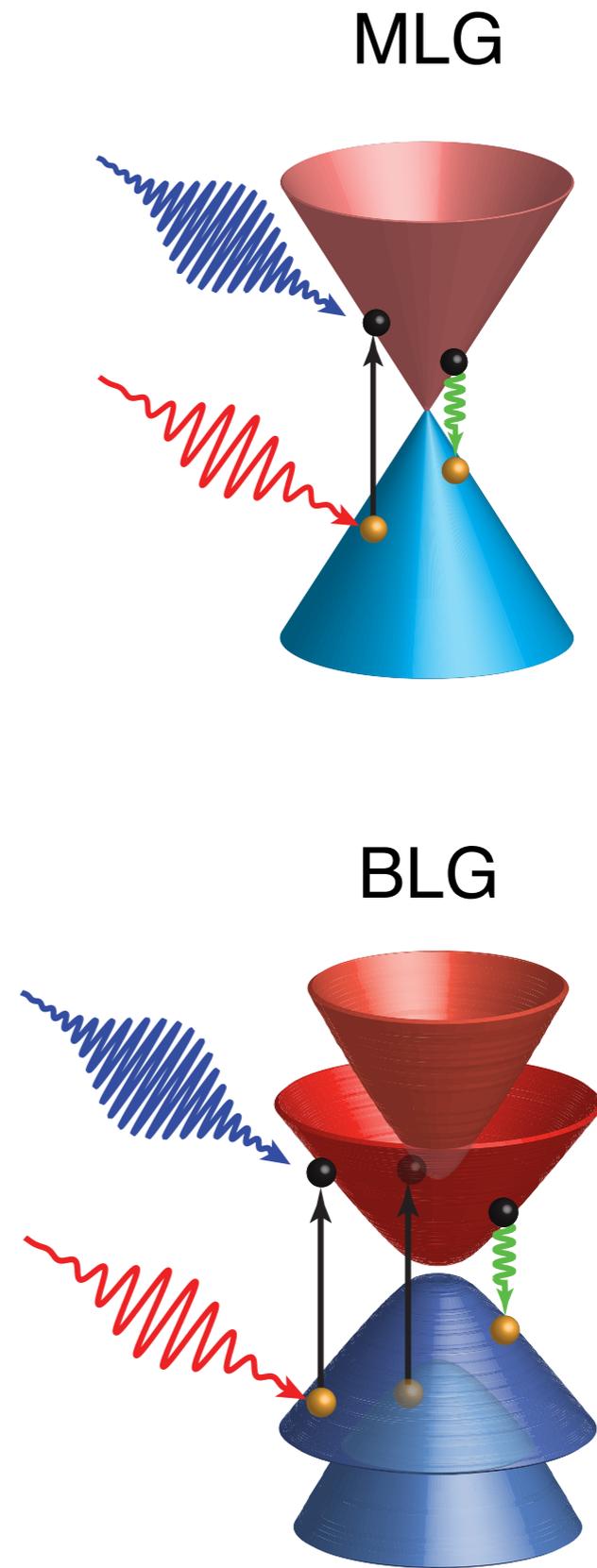
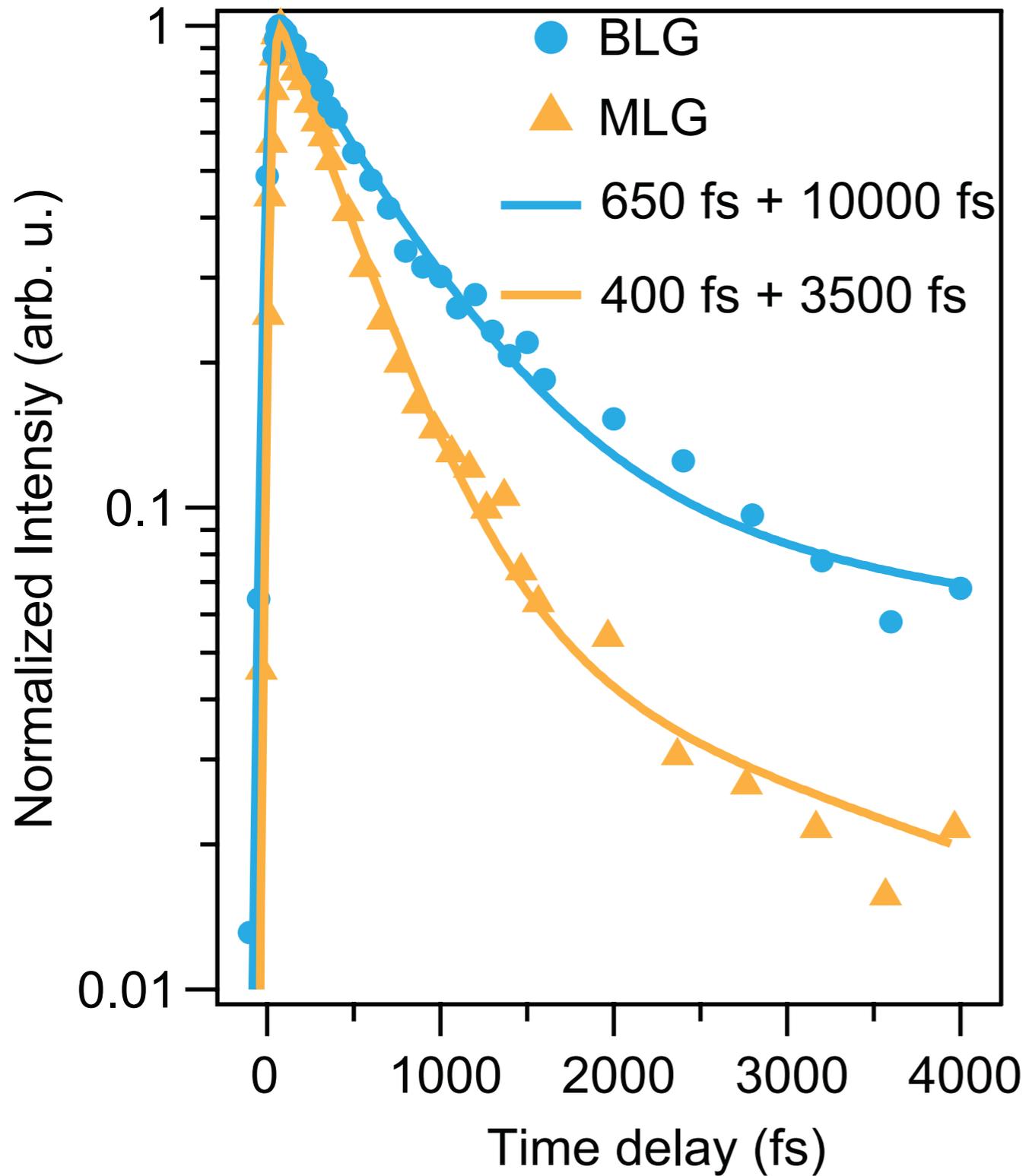
carrier multiplication in n-doped graphene



single layer vs bilayer graphene







Conclusions

- Epitaxial growth permits to grow high quality, large area 2D materials.
- The properties of epitaxial graphene can be widely influenced via intercalation / adsorption-induced confinement.
- The ultrafast electron dynamics in graphene can be observed by time-resolved ARPES. The Dirac cone gives rise to a severe bottleneck for the decay of hot carriers.
- This is even more extreme for bilayer graphene which has a small band gap.

Richard Balog *et al.*, Nature Materials **9**, 315 (2010).

Rosanna Larciprete *et al.* ACS Nano **6**, 9551 (2012).

Silvano Lizzit *et al.*, Nano Letters **12**, 4503 (2012).

Jens Christian Johannsen *et al.*, Physical Review Letters **111**, 027403 (2013).

Søren Ulstrup *et al.*, Physical Review Letters **112**, 257041 (2014).

Jon M. Riley *et al.*, Nature Physics **10**, 835 (2014).

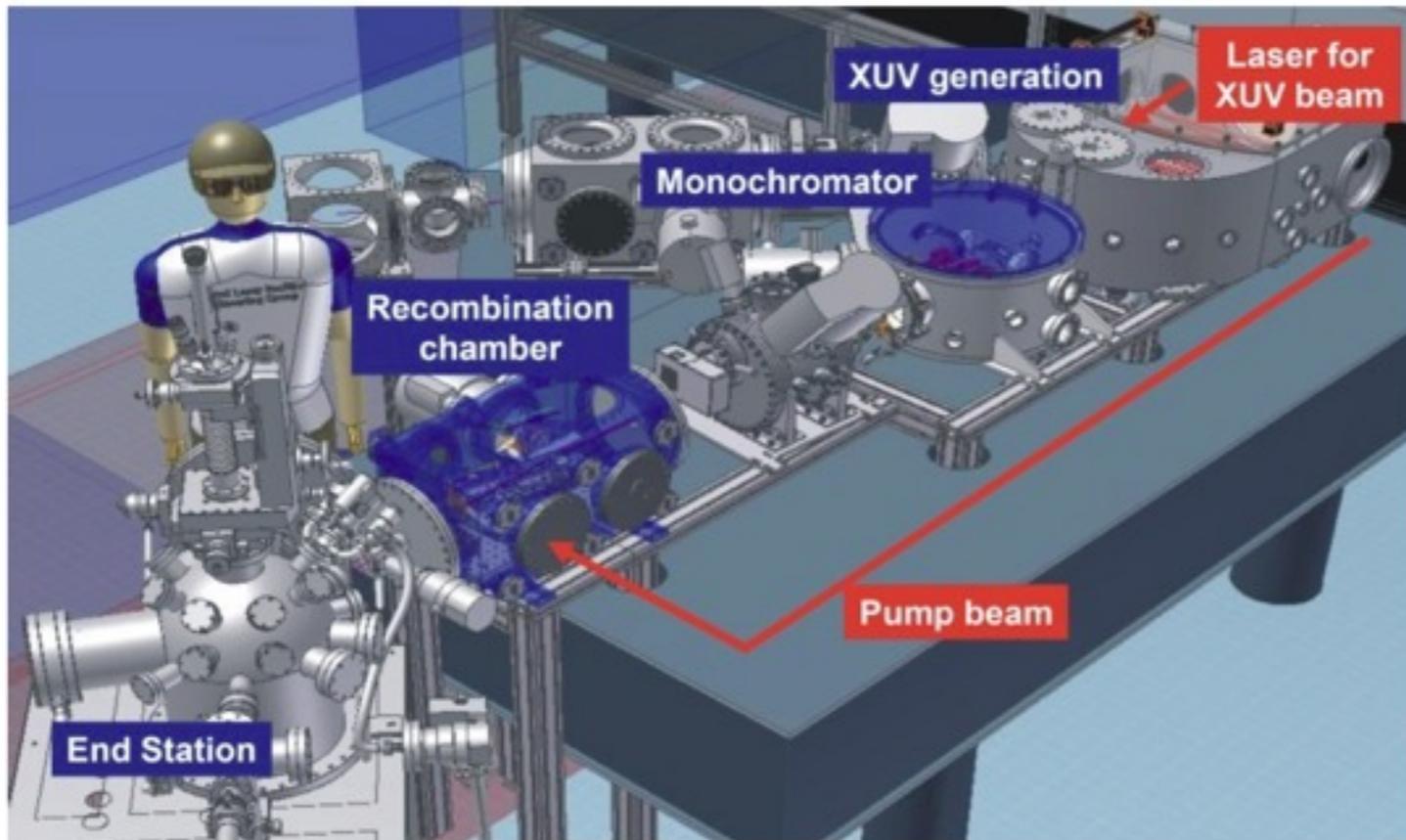
Jill Miwa *et al.*, Phys. Rev. Lett. **114**, 046802 (2015)

Jens Christian Johannsen *et al.*, Nano Letters **15**, 326 (2015).

Extras

ARTEMIS lab

The Artemis Material End Station at the Central Laser Facility /
Rutherford Appleton Laboratory



1 kHz Ti:sapphire laser

Pulse characteristics:

- Wavelength: 785 nm
- Duration: 30 fs
- Energy: 10 mJ

Probe beam

- high harmonic generation (HHG) of XUV pulses in Ar gas cell
- monochromator: 21st Harmonic, $h\nu = 33.2$ eV

Pump beam

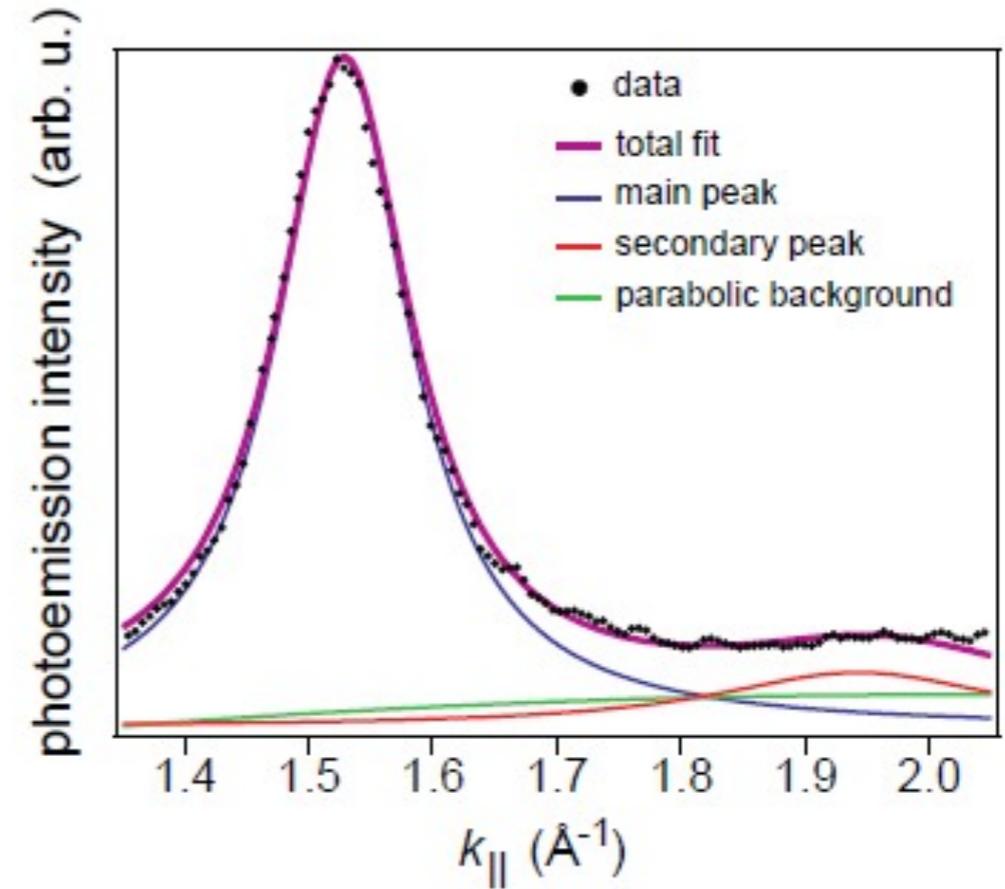
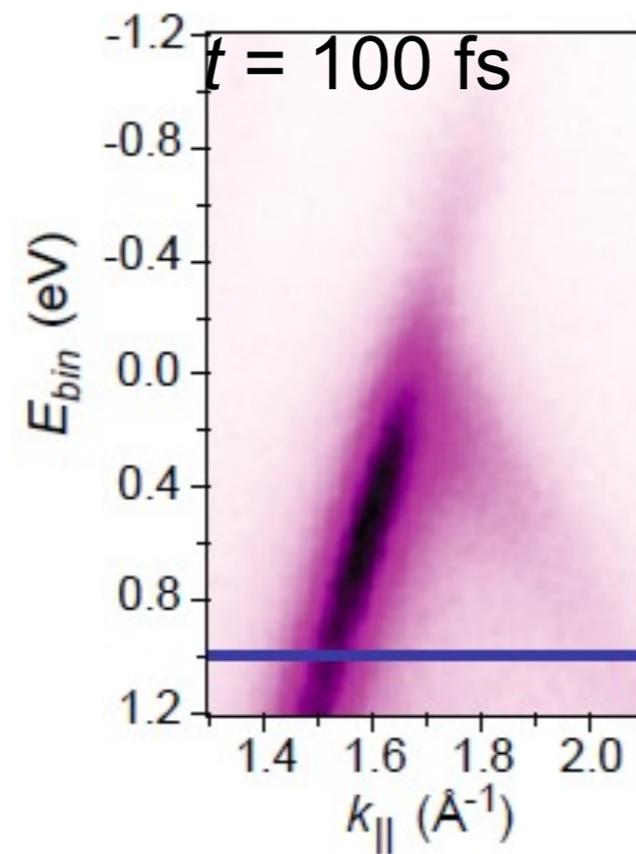
- Tunable pulses with 30 fs duration generated from a OPA (HE-Topas)
- $h\nu = 0.95$ eV
- Fluence: $F = 346 \mu\text{J}/\text{cm}^2$

www.clf.stfc.ac.uk

Frassetto *et al.*, Opt. Express **19** 19169 (2011)

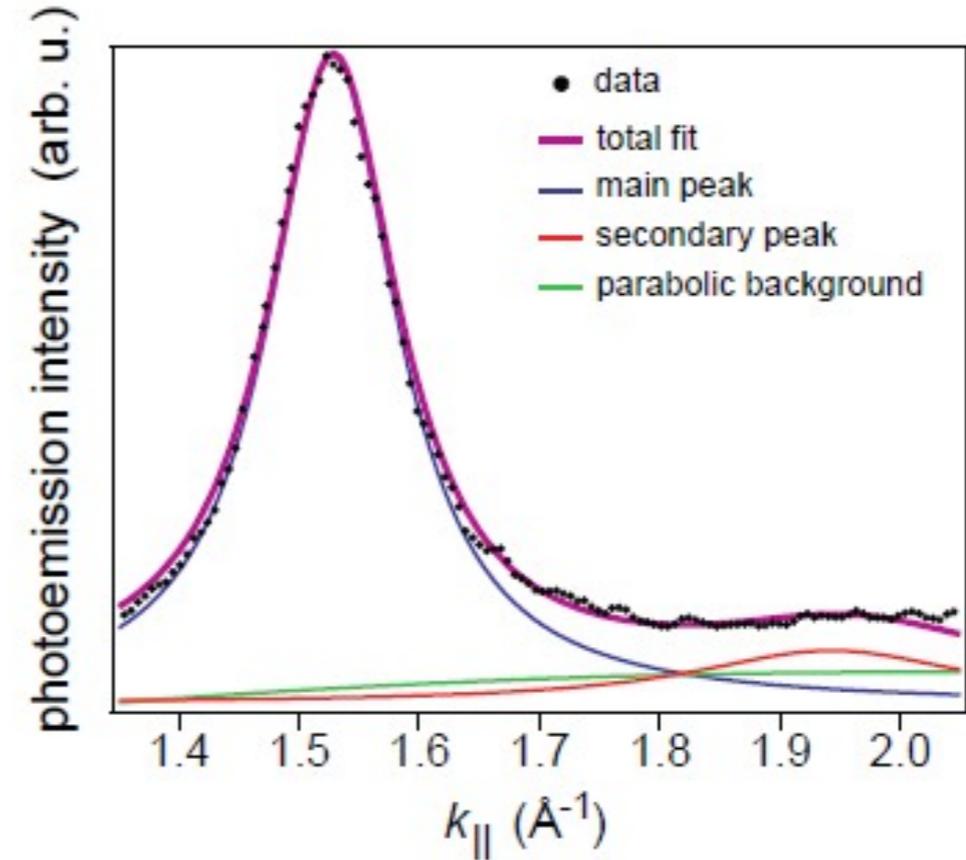
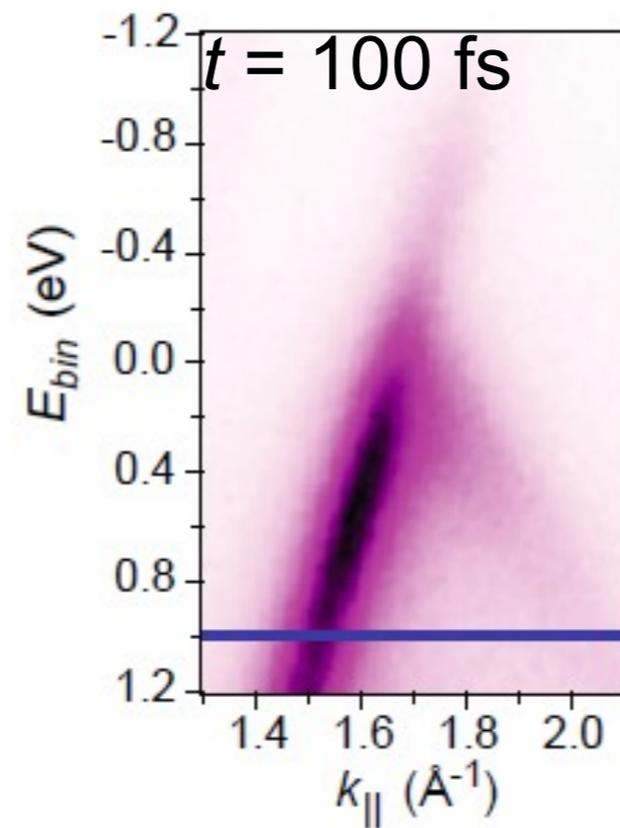
Analysis - extracting the electronic temperature

Fitting momentum distribution curves (MDCs)

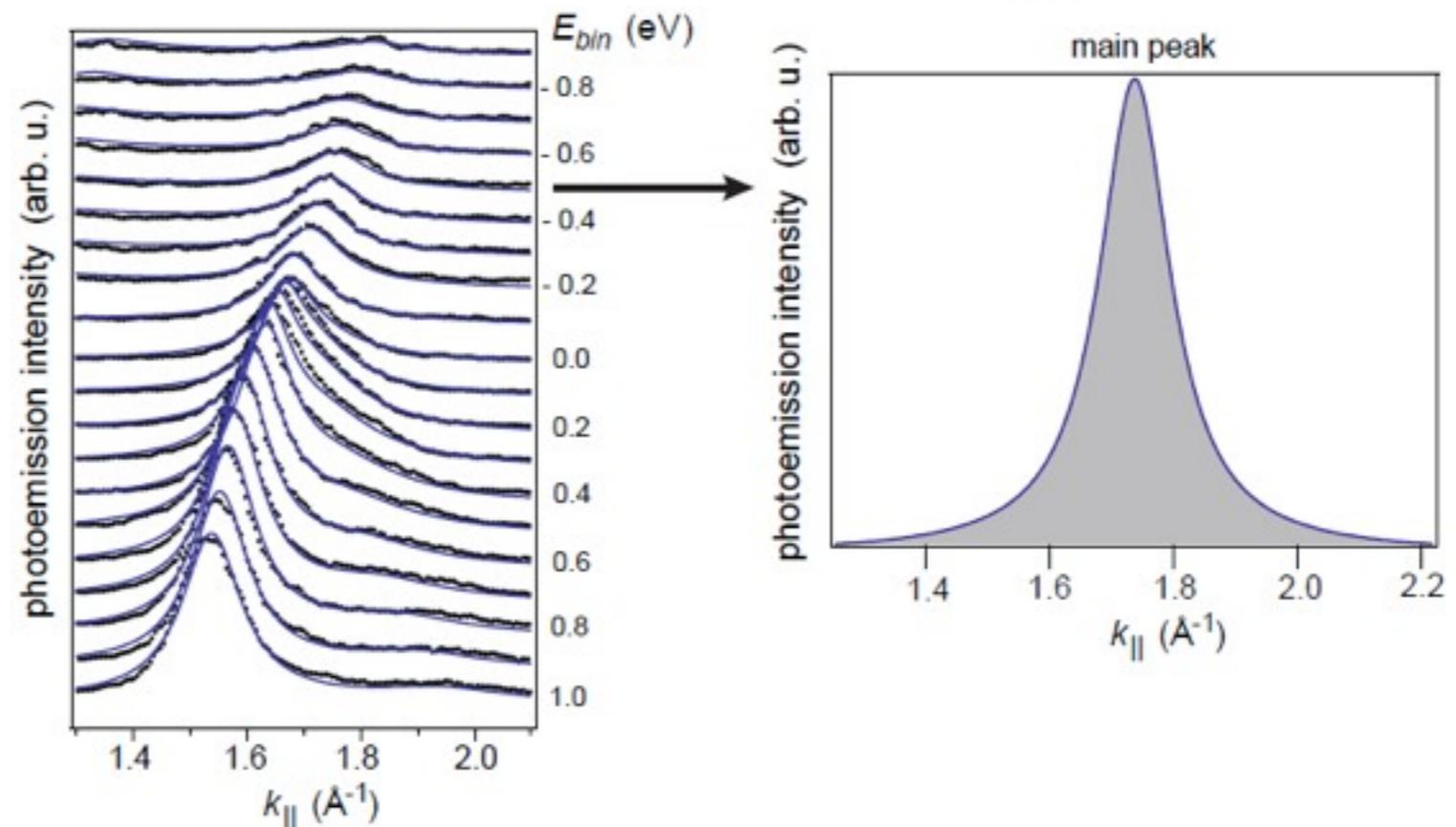


Analysis - extracting the electronic temperature

Fitting momentum distribution curves (MDCs)

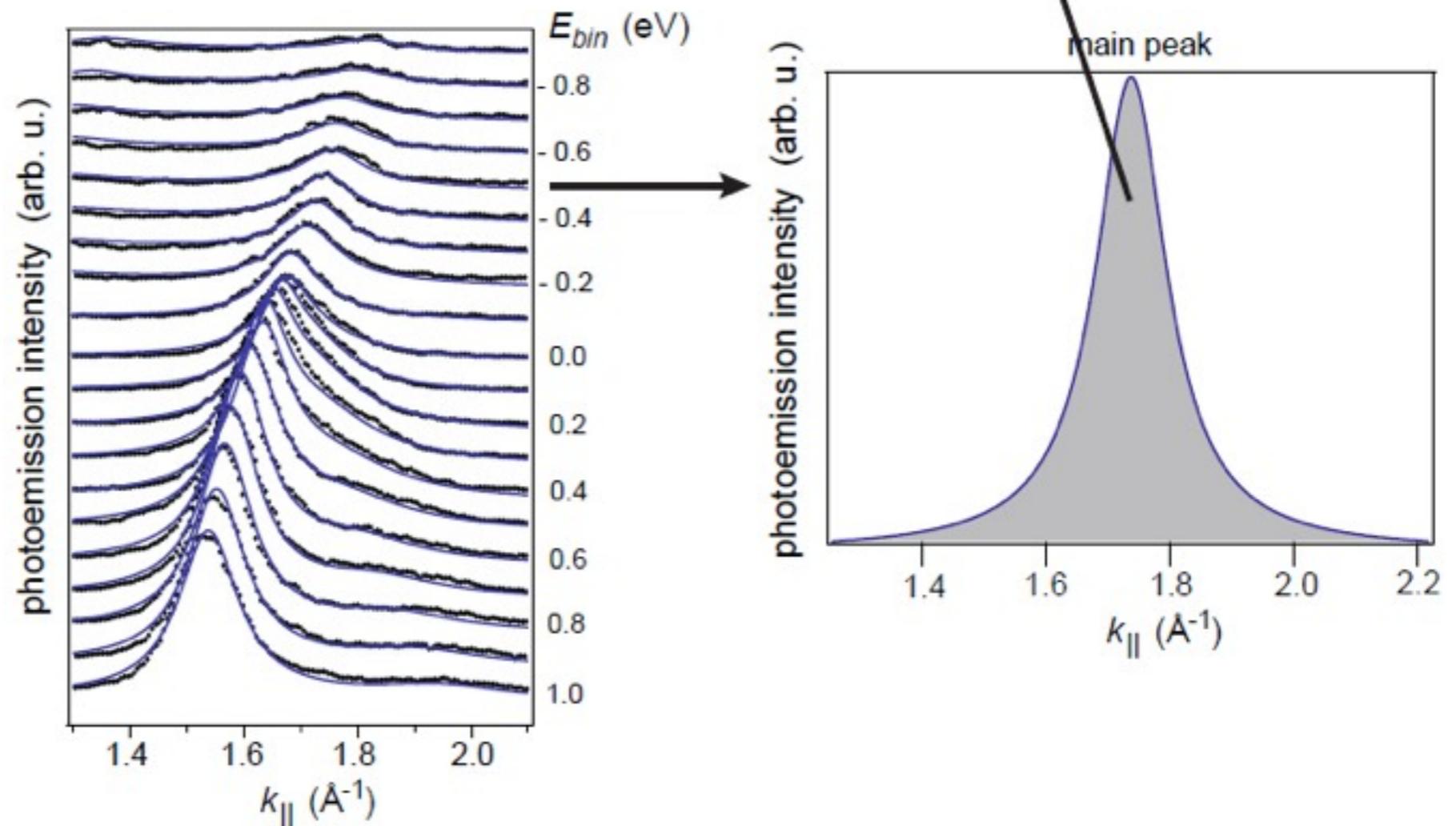
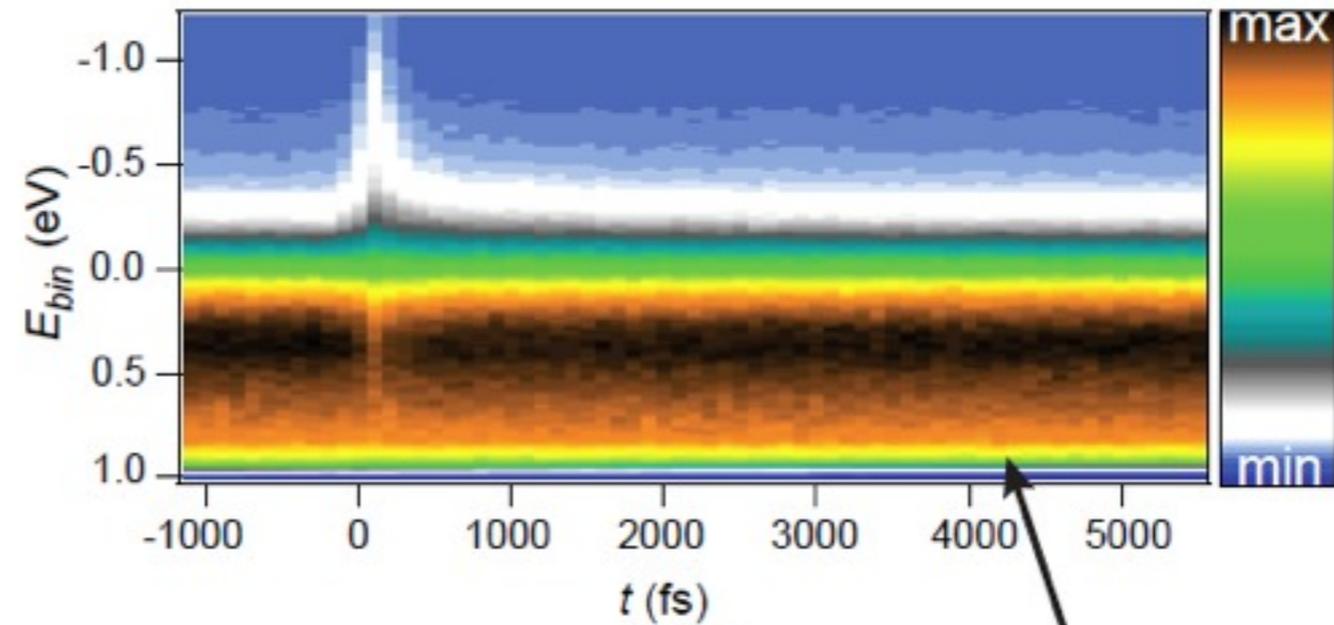


Slice image into 152 MDCs and fit all 67 time delays



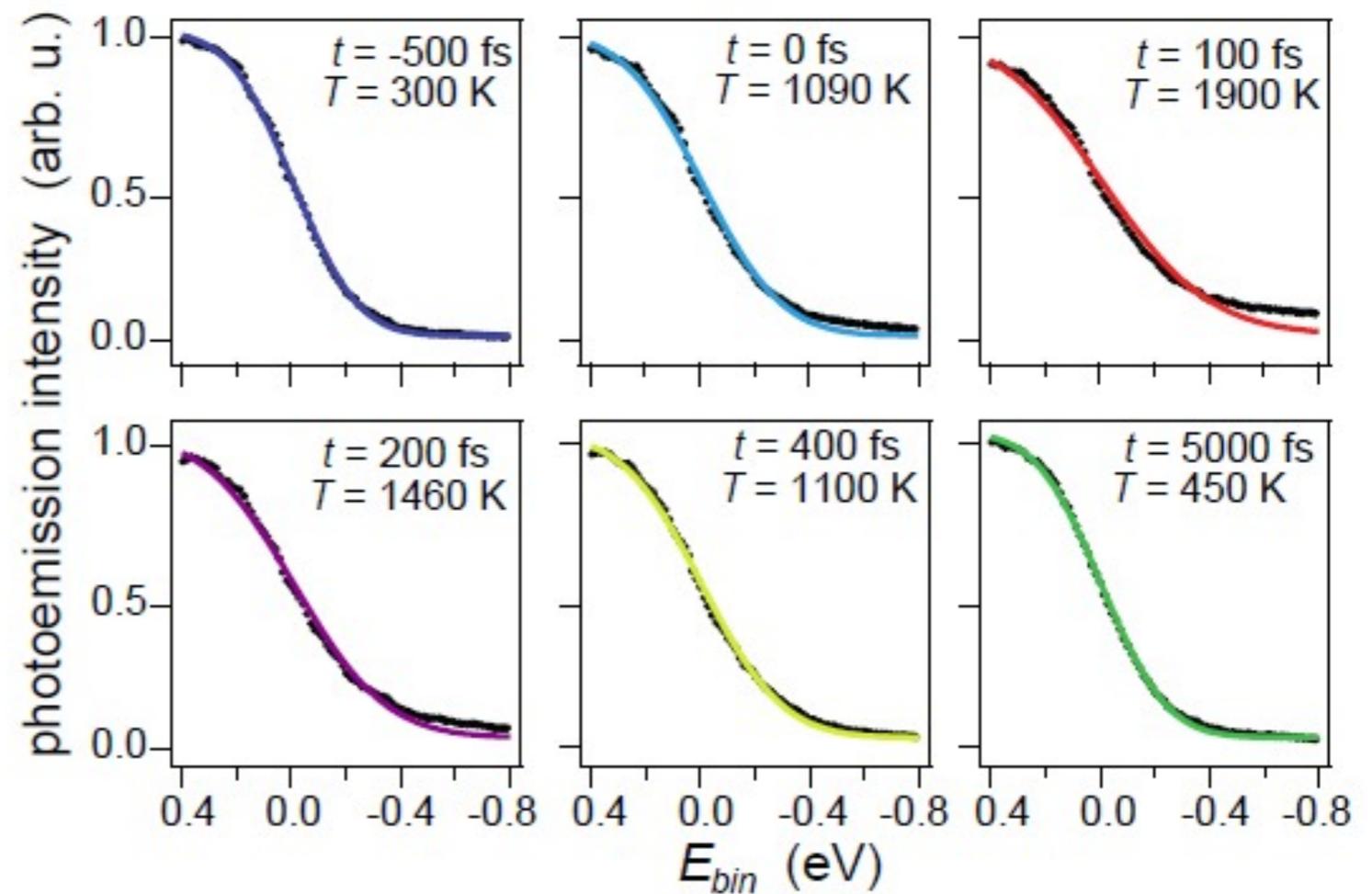
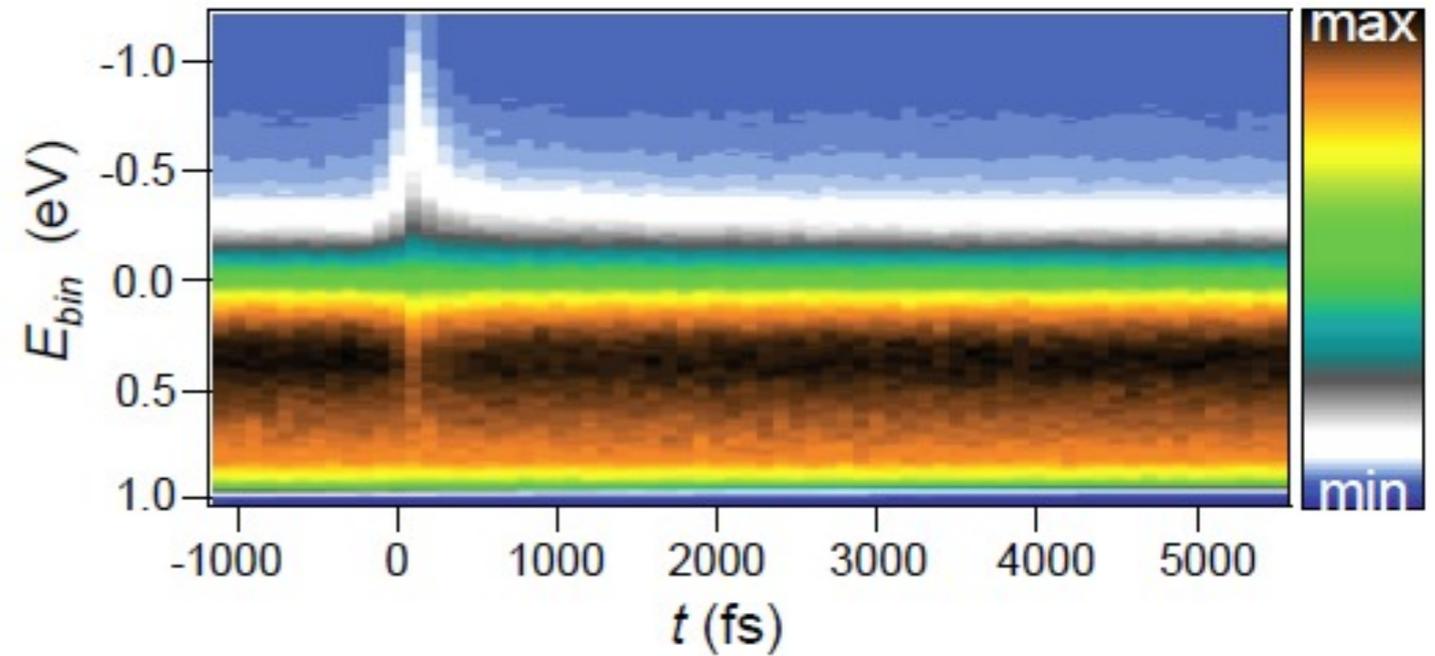
Analysis - extracting the electronic temperature

Integrated peak intensity provides statistical distribution of carriers along the dispersion



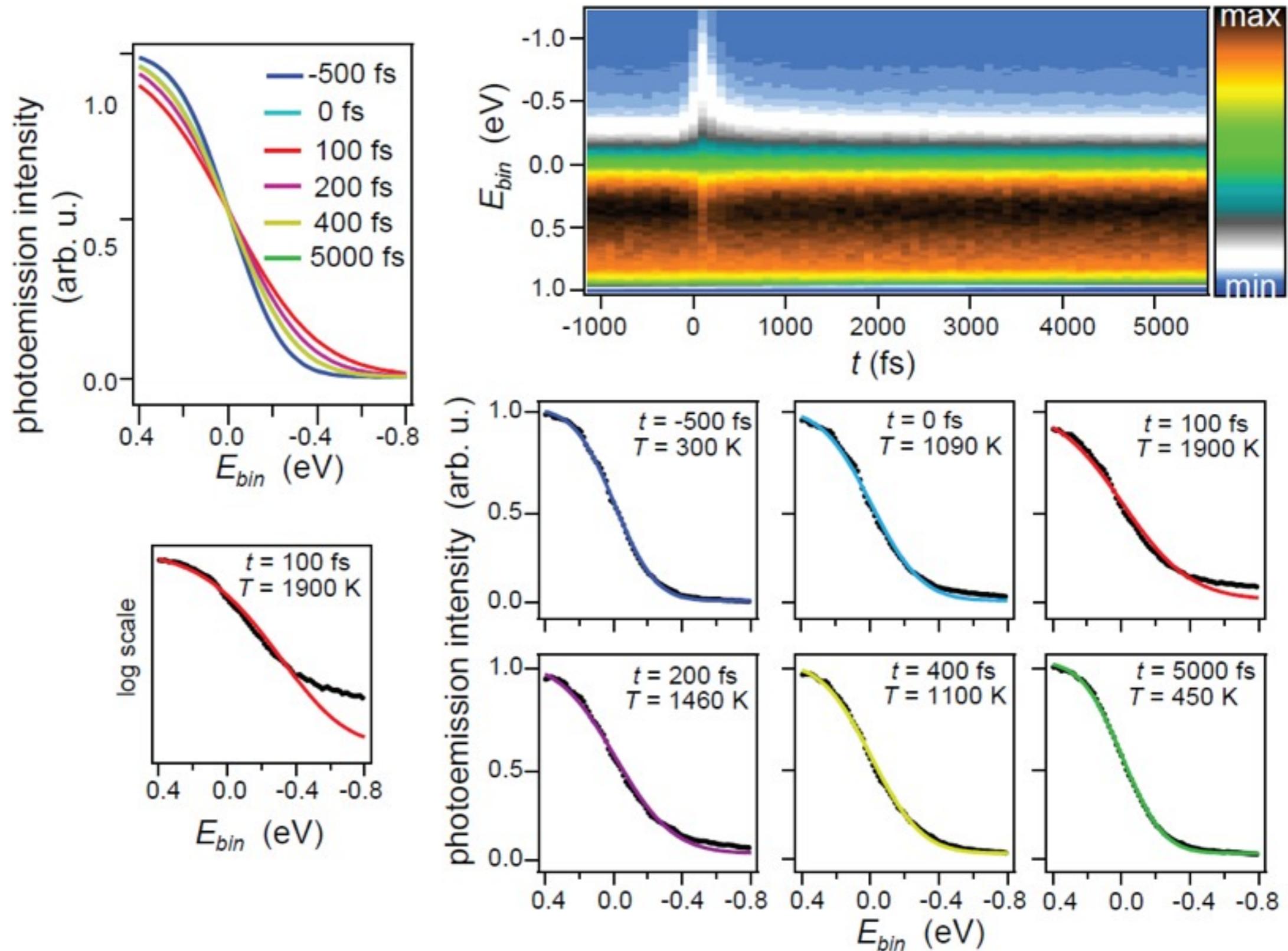
Analysis - extracting the electronic temperature

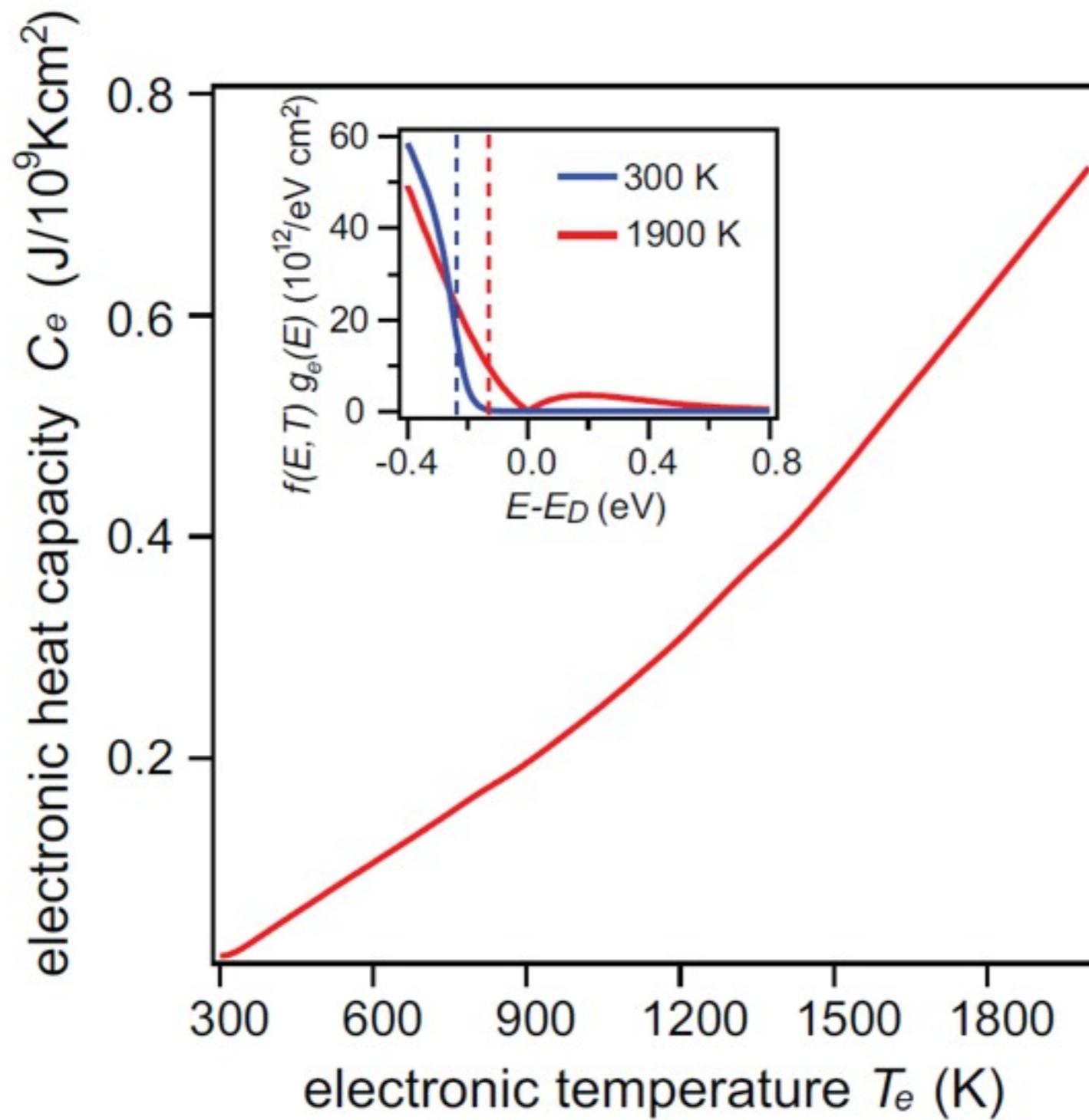
Fitting Fermi-Dirac (FD) distributions



Analysis - extracting the electronic temperature

Fitting Fermi-Dirac (FD) distributions





$$C_e(T) = \frac{d}{dT} \int_{-\infty}^{\infty} g_e(E') f(E', T) E' dE'$$

Changes in valence band

Hole-hole collisions

MDC width decreases immediately after pump excitation

Time dependence of the photohole lifetime:

New scattering channel persisting over 200 fs time scale

